PREPARATION OF ORGANOPHOSPHATE MODIFIED MONTMORILLONITE/POLY(METHYL METHACRYLATE) NANOCOMPOSITE

MR.SANIT SIRAPANICHART
MR.SURALUCK MACKSASITORN
MR.SUWICHA BUAKHEIO

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Student Names	Mr. Sanit Sirapanichart Mr. Suraluck Macksasitorn Mr. Suwicha Buakheio
Department	Chemistry
Program	Petrochemical Technology
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Special Project Advisors	Asst.Prof.Dr. Punnama Siriphannon Asst.Prof.Dr. Pathavuth Monvisade

Abstract

Tetrabutylphosphonium bromide (TBPB) was intercalated into swelled montmorillonite (S-MMT) by cation exchange reaction using 2 modification techniques, i.e., mechanical agitation and sonication. The Phosphonium MMT (P-MMT) was characterized by X-ray diffractometer (XRD), X-ray fluorescence spectrometer (XRF) and thermogravimetric analysis (TGA). The P-MMT obtained from both modification techniques showed the intercalation of phosphonium ions into the 001 plane of S-MMT, resulting in an increase of d_{001} from 1.2 to 1.6 nm. The amount of intercalated phosphonium ions in the P-MMT was about 5.6 wt%. The degradation temperature of intercalated TBPB was higher than raw TBPB for 20 °C. The P-MMT was used for preparation of PMMA/P-MMT nanocomposite film. The amount P-MMT in the composites was varied, i.e., 1, 2, 3, and 6 wt%. The higher P-MMT loading, the higher thermal stability was obtained in the PMMA/P-MMT film. In addition, the absorbance of UV-A and UV-B of PMMA/P-MMT film were higher than those of the PMMA, suggesting that the PMMA/P-MMT could be used as the UV-screening film for the windscreen and the glasses lens.

ACKNOWLEDGMENTS

The author would like to take this opportunity to express sincere thanks to their advisors and people who gave useful advice and full support in this research.

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They also would like to give the special thanks to all of their friends at department of science who have been helping and encouraging them while studying at King Mongkut's Institute of Technology Ladkrabang.

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Mr.Sanit Sirapanichart
Mr.Suraluck Macksasitorn
Mr.Suwicha Buakheio

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Chapter 1
Introduction

1.1 Introduction

Organoclays have attracted substantial attention both in fundamental research and industrial applications because of their superior reinforcement properties, [20],[21],[26], such as polymer–clay nanocomposites [37-39], absorbents of organic pollution in ground water, coatings and paints [40-44]. Each clay particle consists of silicate layers which are around 1 nm thick [37-39]. The surface properties of organoclays are very important for their applications. For example, organoclays vary in the selectivity of adsorbing one organic compound over another and in the amount of adsorbed organic materials, as shown by adsorption isotherms [45]. Compared to conventional filled polymers, clay/polymer nanocomposites can have enhanced mechanical properties, increased heat distortion temperature, improved thermal stability, decreased gas/vapor permeability and reduced flammability [23],[24], [28-30].

Several methods have been reported to synthesize clay/polymer nanocomposites; however, three methods (in situ polymerization, intercalation in solutions and melt processing) developed during the early stages of this field are widely applied [23]. The melt processing technique is mostly used because this process played an important role in speeding up the progress of the commercial production of clay/polymer nanocomposites.

Most of the commercially available organoclays are produced by exchange of alkali or alkali earth cations in the interlayer space of clay minerals, such as montmorillonite (MMT, a commonly used layered silicate), with alkyl ammonium salts [23-25],[28]. Other cations, such as phosphonium, pyridinium and imminium have also been used due to their higher thermal stability [30]. Alkyl ammonium modified clays are thermally not very stable above 250 °C and start to degrade at

nanocomposites processing temperature (200–300 °C). Therefore, organoclays prepared using quaternary alkyl ammonium salts are less suitable for most engineering plastics with high processing temperature [22],[27],[31-35].

Phosphonium compounds are widely used as stabilizers in many applications and offer unique additional opportunities for polymer-layered silicate nanocomposites [36]. For example, mono- and bisphosphonium salts are used as flame retardants for textiles and paper, stabilization agents for polyacrylonitrile fibers exposed to sunlight, heat stabilizers for nylon, and condensation additives to organic dyes to produce wash-fast colors. Thus, the use of phosphonium salts as organic modifiers to layered silicates may further enhance the thermal and flammability properties of polymer nanocomposites.

The thermal stability of organoclays is improved by intercalating quaternary phosphonium salts [34]. Degradation pathways and thermal stability depend on molecular structure. Nevertheless, the stability of phosphonium MMT is substantially decreased (70–80 °C) with regard to the parent phosphonium salt, necessitating future studies of the specific influence of the interlayer environment and aluminosilicate surface on reaction pathways.

In this study, the preparation and characterization of phosphonium MMT (P-MMT) by the interaction of tetrabutylphosphonium bromide (TBPB) with MMT were investigated. The modification technique of organoclay was interested in the different preparation method, agitation and sonication. Then the P-MMT was examined to apply as an additive in poly(methyl methacrylate), (PMMA), formed a PMMA/ P-MMT film by spinning on a glass substrate. The solvent screening, spinning on a glass substrate and characterization of PMMA/P-MMT film preparation were concerned.

1.2 Objectives

1.2.1 To study and investigate the suitable method for modification of montmorillonite with phosphonium salt.

1.2.2 To prepare poly(methyl methacrylate)/modified montmorillonite nanocomposite film.

1.2.3 To study the properties of PMMA/P-MMT film that affected by amount of P-MMT.

1.3 Scope of study

1.3.1 Preparation of organoclay filler from MMT and TBPB by weight ratio 2:0.72 using mechanical stirrer and sonication techniques.

1.3.2 Characterization of P-MMT by using X-ray diffractometer (XRD), X-ray fluorescence spectrometer (XRF) and thermogravimetric analysis (TGA) techniques.

1.3.3 Synthesis of PMMA by solution polymerization of MMA monomer.

1.3.4 Molecular weight of PMMA is analyzed by using gel permeation chromatographer (GPC) technique.

1.3.5 Undergoing the solvent screening of PMMA by using dichloromethane, xylene and toluene as a solvent.

1.3.6 Preparation of PMMA/ P-MMT film by spinning on a glass substrate.

1.3.7 Characterization of PMMA/P-MMT film by using XRD, TGA and UV-vis techniques.

1.4 Expected results

1.4.1 The modification of S-MMT with TBPB by intercalation can be successfully in the best way for preparation.

1.4.2 The benefits of PMMA/P-MMT film can be applied for the industrial purposes in the future.

Chapter 2
Theory and Literature Reviews

2.1 Clays and Clay Modifications [1-5]

Clay is a soil composed of hydrous aluminium phyllosilicate minerals and has a particle size that is typically defined as less than 2 μm in diameter. Clay consists of a variety of phyllosilicate minerals rich in silicon and aluminium oxides and hydroxides which include variable amounts of structural water. Clays are generally formed by the chemical weathering of silicate-bearing rocks by carbonic acid, but some are formed by hydrothermal activity. Clays are distinguished from other small soil particles, such as silt, by their smaller size, flake or layered shape, affinity for water and tendency toward high plasticity.

2.1.1 The physical characteristics of clays [2]

- Clay minerals tend to form microscopic to sub microscopic crystals.
- They can absorb water or lose water from simple humidity changes.
- When mixed with limited amounts of water, clays become plastic and are able to be molded and formed.
- When water is absorbed, clays will often expand as the water fills the spaces between the stacked silicate layers.
- Due to the absorption of water, the specific gravity of clays is high variable and is lowered with increased water content.
- The hardness of clays is difficult to determine due to the microscopic nature of the crystals, but the hardness is usually about 2-3 and many clays give a hardness of 1 in field tests.
- Clays tend to form from weathering and secondary sedimentary processes with only a few examples of clays forming in primary igneous or metamorphic environments.
- Clays are rarely found separately and are usually mixed not only with other clays but with microscopic crystals of carbonates, feldspars, micas and quartz.

2.1.2 Grouping

Depending upon academic source, there are three or four main groups of clays:

- Kaolinite [$Al_2Si_2O_5(OH)_4$]
- Montmorillonite-smectite [$(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2 - nH_2O$]*
- Illite [Clay-mica, $(K, H)Al_2(Si, Al)_4O_{10}(OH)_2 - nH_2O$]*
- Chlorite

Chlorites are not always considered clay, sometimes being classified as a separate group within the phyllosilicates. There are approximately thirty different types of "pure" clays in these categories, but most "natural" clays are mixtures of these different types, along with other weathered minerals.

*(*where n represents the variable amount of water)*

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. It is named after montmorillon in France. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately 1μm.

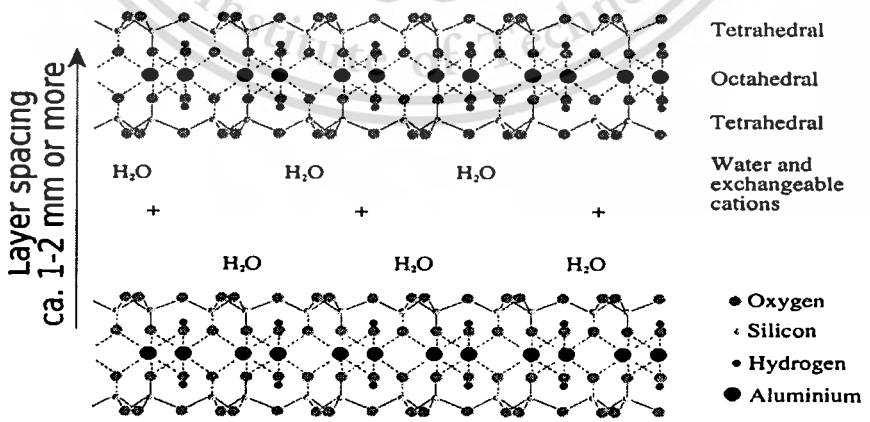


Fig. 2.1 Structure of Montmorillonite

It is the main constituent of the volcanic ash weathering product, bentonite.

Montmorillonite has a crystalline structure. It results in a "flake" particle shape that resembles a corn flake. These flakes are extremely small, ranging in long dimension from 10 micrometers to 0.01 micrometers. Hundreds of such flakes aggregate to form a thin particle. One gram of montmorillonite has a surface area 750 m^2/g, nearly as much as the best activated carbon grains. Twelve grams have a surface area that covers an entire football field. This variance in thickness is related to the adsorption of water and other polar molecules.

Fig. 2.2 Flake particle shape that resembles a corn flake of montmorillonite

The material is always electrically unbalanced by substitutions, such as magnesium, iron, or calcium replacing aluminum. This results in a charge deficiency that must be balanced externally by cations, which in turn are exchangeable. The quantity of cations required to create a net charge balance is called "*the exchangeable cation capacity*." The internal charge deficiency inside it results in a net negative charge of the particle, which in turn is compensated for by exchangeable cations positioned but weakly held near the tetrahedral layers. The most prominent cations are sodium, calcium, magnesium, and potassium, respectively.

The exchangeability of these cations allows this material to remove heavy metals from water, an important consideration for wastewater treatment. Simultaneously, it removes cationic organics by ion exchange, resulting in an interaction with polymers. Its large swelling capacity, combined with ion exchange capacity, allows the material to form a floc with suspended solids that can be precipitated out of the water.

The combination of the relative purity, its unusual geochemistry and structure is why the material is unique to this area of the world is an extremely high quality material. Purity is defined by the amount of sodium montmorillonite as compared to the other minerals present. A typical sample contains up to 90% montmorillonite while other similar materials produced around the world have only 70-80% montmorillonite.

The color of the material can range from white to light olive green, cream, yellow, earthy red, brown and sometimes sky blue when fresh but yellowing rapidly with exposure to air. When wet it is highly plastic and slippery, often appearing greasy or waxy.

Montmorillonite's water content is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. Potassium, iron, and other cations are common substitutes; the exact ratio of cations varies with source. It often occurs intermixed with chlorite, muscovite, illite, cookeite and kaolinite.

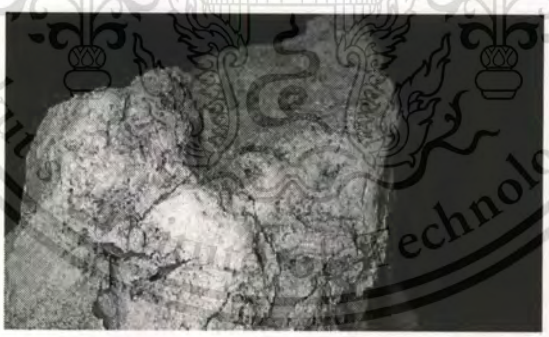


Fig. 2.3 Sample of montmorillonite *(unknown scale)*

Montmorillonite is used in the oil drilling industry as a component of drilling mud, making the mud slurry viscous which helps in keeping the drill bit cool and removing drilled solids. It is also used as a soil additive to hold soil water in drought prone soils, to the construction of earthen dams and levees and to prevent the leakage of fluids. It is also used as a component of foundry sand and as a desiccant to remove moisture from air and gases.

Similar to other clays, montmorillonite swells with the addition of water. However, some montmorillonites expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. The amount of expansion is due largely to the type of exchangeable cation contained in the sample. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times its original volume. Hence, sodium montmorillonite has come to be used as the major constituent in non-explosive agents for splitting rock in natural stone quarries in order to limit the amount of waste, or for the demolition of concrete structures where the use of explosive charges is unacceptable.

Montmorillonite has been used in cosmetics and has reputed therapeutic effects. Indeed over 200 cultures have used the clay for medicinal purposes including the Ancient Egyptians, the Essenes and the pre-Aztec Amargosians, and other natives of Mexico, South America and North America.

Montmorillonite is also used in animal feeds as an anti-caking agent. Current research indicates that montmorillonite or bentonite has the ability to bind mycotoxins in the digestive system of animals as well as several bacteria in-vitro.

It is known for its adsorbent qualities and has been used successfully in scientific trials to eliminate atrazine from water.

2.2 Composite [18]

There are two categories of constituent materials: matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. Engineered composite materials must be formed to shape. The matrix material can be introduced to the reinforcement before or after the reinforcement material is placed into the mold cavity or onto the mold surface. The matrix material experiences a

melding event, after which the part shape is essentially set. Depending upon the nature of the matrix material, this melding event can occur in various ways such as chemical polymerization or solidification from the melted state.

2.3 Nanocomposite [6,9]

Nanocomposite is a type of composites containing filler that has at least one dimension in the range of nanometer. Most of the nanocomposites can be produced by using metal particles, colloids, and smectic-clay minerals. Nanotechnology has gained interest in the development such as polymer nanocomposite, typically, smectic-clay are used as fillers. Montmorillonite and hectorite layered structure are dispersed in polymer matrix.

Dispersion of clay minerals in a polymer matrix is categorized into three types, i.e., conventional composite, intercalated nanocomposite and exfoliated nanocomposite. *Conventional composite* contains the existing clay tactoids in original aggregated state with a non-intercalated polymer chain along the silicate layers. The clay tactoids are simply dispersed as a segregate phase. *Intercalated nanocomposite* is formed by the insertion of one or more polymer chains into the clay galleries resulting in a well ordered multilayer with alternating polymer chains and nanoscale inorganic layers, owing to the spatial confinement of the polymer between the dense clay layers. Intercalated polymer-clay nanocomposites can exhibit impression conductivity. *Exfoliated nanocomposite* can be obtained by separating a single silicate layer in the polymer matrix with the average distance of each layer depending on the clay content. The clay contents in exfoliated nanocomposite are usually much lower than in intercalated one. In addition, the non-dispersed hybrid corresponds to a conventional composite whereas the fine dispersed hybrid corresponds to either an intercalated or and exfoliated nanocomposite.

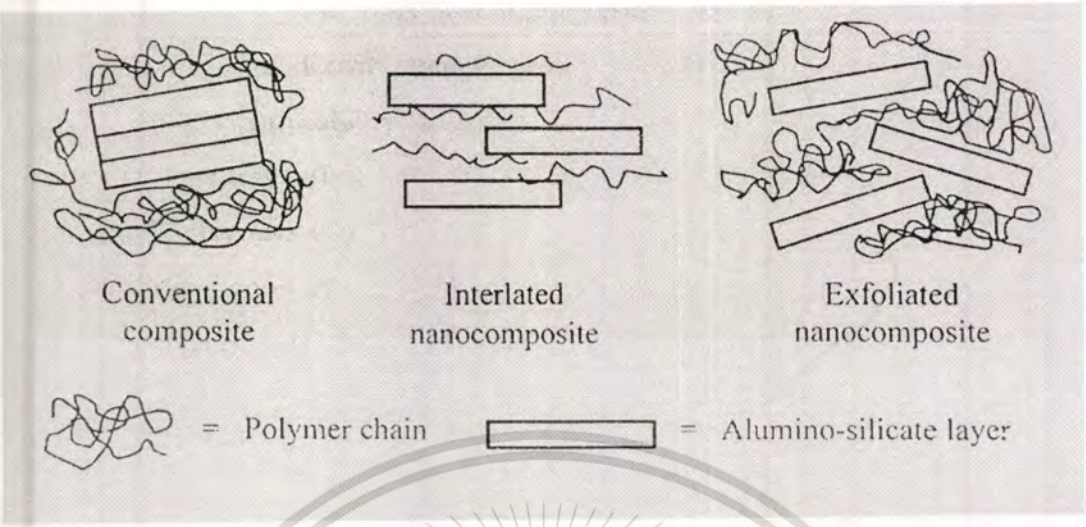


Fig. 2.4 Types of polymer-clay composites; (A) conventional composite, (B) intercalated nanocomposite and (C) exfoliated nanocomposite

The clay-containing polymeric nanocomposite performance is the extent of intercalation and exfoliation, X-ray diffraction (XRD) is the principal method that has been used to examine this [46]. The presence of multiple peaks in XRD spectra is quite common – it often originates from different organoclay structures and its incomplete change during incorporation in a polymeric matrix [47].

For the interlayer spacing, d_{001}, normally shown at low θ in the XRD pattern, is commonly determined from the XRD spectrum as arbitrary intensity versus 2θ. The spacing is then calculated from Bragg's law:

$$n\lambda = 2(d_{001})\sin\theta$$

where n is an integer, θ is the angle of incidence (or reflection) of the X-ray beam, and λ is the X-ray wavelength most X-ray machines use Cu-$K\alpha_1$ radiation with λ = 0.1540562 nm. The peak position and the interlayer spacing related to the equation is one part of the information provided by XRD measurements. The intensity of the diffraction peak and its dependence on the concentration of scattering particles yields other information.

2.4 Cation Exchange Capacity (CEC)[7]

The cation exchange capacity (CEC) is a value given on a soil analysis report to indicate its capacity to hold cation nutrients. The CEC, however, is not something that is easily adjusted. It is a value that indicates a condition or possibly a restriction that must be considered when working with that particular soil. Unfortunately CEC is not a packaged product. The two main colloidal particles in the soil are clay and humus and neither are practical to apply in large quantities.

The CEC of the soil is determined by the amount of clay and/or humus that is present. These two colloidal substances are essentially the cation warehouse or reservoir of the soil and are very important because they improve the nutrient and water holding capacity of the soil. Sandy soils with very little organic matter (OM) have a low CEC, but heavy clay soils with high levels of OM would have a much greater capacity to hold cations.

The disadvantages of a low CEC obviously include the limited availability of mineral nutrients to the plant and the soil's inefficient ability to hold applied nutrients. Plants can exhaust a fair amount of energy (that might otherwise have been used for growth, flowering, seed production or root development) scrounging the soil for mineral nutrients. Soluble mineral salts (e.g. Potassium sulfate) applied in large doses to soil with a low CEC cannot be held efficiently because the cation warehouse or reservoir is too small.

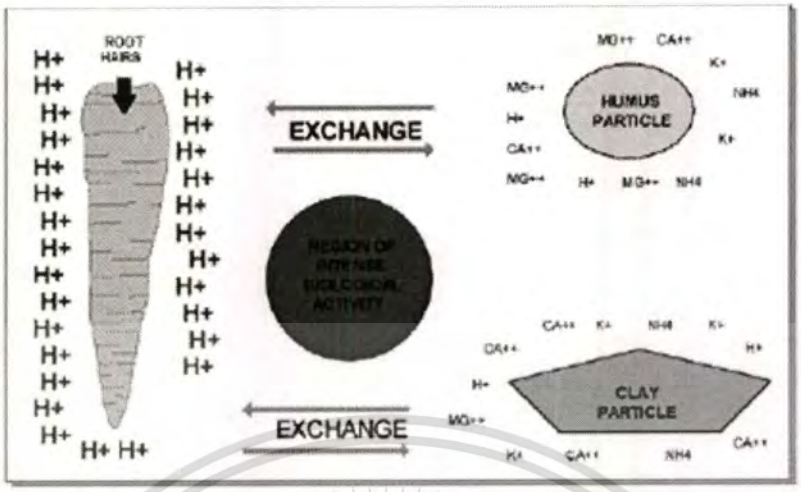


Fig. 2.5 Cation exchange

Water also has a strong attraction to colloidal particles. All functions that are dependent on soil moisture are also limited in soils with low CEC. Organisms such as plants and microorganisms that depend upon each other's biological functions for survival are inhibited by the lack of water. Where there is little water in the soil, there is oftentimes an abundance of air which can limit the accumulation of organic matter (by accelerating decomposition) and further perpetuate the low level of soil colloids.

High levels of clay with low levels of OM would have an opposite effect (i.e. a deficiency of air), causing problems associated with anaerobic conditions. The CEC in such a soil may be very high, but the lack of atmosphere in the soil would limit the amount and type of organisms living and/or growing in the area, causing dramatic changes to that immediate environment.

If a soil has a very low CEC, adjustments can and should be made but not solely because of the CEC. A soil with a very low CEC has little or no clay or humus content. Its description may be closer to sand and/or gravel than to soil. It cannot hold very much water or cation nutrients and plants cannot grow well. The reason for the necessary adjustment is not for the need of a higher CEC but because the soil needs conditioning. A result of this treatment is higher CEC.

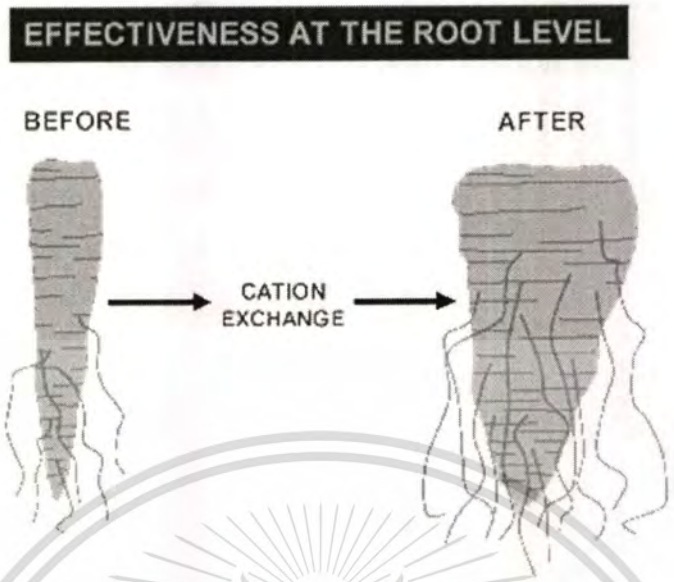


Fig. 2.6 Effectiveness of cation exchange at the root level

2.5 Organophosphorus [8]

Organophosphorus compounds are chemical compounds containing carbon-phosphorus bonds. Organophosphorus chemistry is the corresponding science exploring the properties and reactivity of organophosphorus compounds. Phosphorus shares group 15 in the periodic table with nitrogen and phosphorus compounds and nitrogen compounds have much in common.

Phosphorus can adopt oxidation states −3, −1, 1, 3 and 5, oxidation state +5 are of great technological importance as flame retardant *agents and* plasticizers. In chemical literature very often compounds with +3 or −3 oxidation state are grouped together as having a (III) oxidation state regardless of sign. In an official and more descriptive nomenclature phosphorus compounds are identified by their coordination number δ and their valency λ. In this system a phosphine is a $\delta^3\lambda^3$ compound.

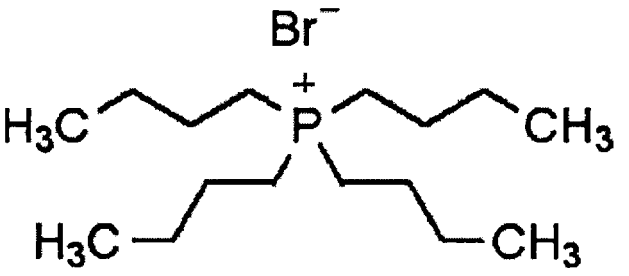


Fig. 2.7 Tetrabutylphosphonium bromide

Along with the well-known properties of phosphorus compound, such as flame retardancy and heat stabilization, many of researches are developed, e.g.

Hasmukh A. Patel, Rajesh S. Somani, Hari C. Bajaj, Raksh V. Jasra [19], 2006, studied on Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. Quaternary phosphonium cations (hexadecyl tributyphosphonium; tetradecyl tributylphosphonium; tetraphenylphosphonium; methyl triphenylphosphonium; ethyl triphenylphosphonium and propyl triphenylphosphonium) were intercalated into montmorillonite (MMT) rich bentonite of Indian origin, by ion exchange reaction. The phosphonium MMT were characterized by Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction analysis (PXRD), particle size distribution (PSD) and thermogravimetric analysis (TGA). The phosphonium cations significantly influenced the particle size distribution. With longer alkyl chain finer particles were formed. The tetrabutylphosphonium and tetraphenylphosphonium MMT showed enhanced thermal stability (300–400 °C) and may be potentially useful materials for melt processing of polymer/layered silicates nanocomposites.

Wei Xie, Rongcai Xie, Wei-Ping Pan, Doug Hunter, Bryan Koene, Loon-Seng Tan, and Richard Vaia [10], 2002, studied on the thermal stability of quaternary phosphonium modified montmorillonites. Organically modified layered silicates (OLS) with high thermal stability are critical for synthesis and processing of polymer layered silicate nanocomposites (PLSN). In the current study, the non-oxidative thermal degradation chemistry of alkyl and aryl quaternary phosphonium-modified

montmorillonites (P-MMT) was examined using TGA combined with pyrolysis/GC-MS. The morphology evolution at elevated temperature was investigated using in-situ high-temperature X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The onset decomposition temperature via TGA of these P-MMTs ranged from 190 to 230 °C. The initial degradation of the alkyl P-MMTs follows potentially two reaction pathways - *â*-elimination [E*â*] and nucleophilic displacement at phosphorus [SN(P)] - reflecting the multiple environments of the surfactant in the silicate. Aryl P-MMT decomposition proceeds via either a reductive elimination through a five-coordinate intermediate or radical generation through homologous cleavage of the P-phenyl bond.

Overall, the interlayer environment of the montmorillonite has a more severe effect on stability of the phosphonium surfactant than previously reported for ammonium-modified montmorillonite (N-MMT). Nonetheless, the overall thermal stability of P-MMT is higher than that of N-MMT. These observations indicate that, in addition to their conventional purpose as stabilizers, phosphonium salts offer unique opportunities for melting processing polymer layered silicate nanocomposites.

Youngchul Lee, Myeong-Jun Kim, and Yong-Bong Lee [11], 2007, concerned in preparation and characterization of epoxy/clay nanocomposites. Epoxy/clay nanocomposites have been prepared using Montmorillonite (MMT) ion-exchanged with various organic cations; hexadecyltributyl phosphonium ion, octadecyltrimethyl ammonium ion, methyl tallow bis-2-hydroxyl ammonium ion and dimethyl hydrogenated tallow (2-ethylhexyl) ammonium ion. The resulting nanocomposites were found to show exfoliated clay structure by using transmission electron microscope (TEM) and X-ray diffractometry (XRD). The flame retarding property of 5wt% clay/epoxy nanocomposites was found to be enhanced when compared with that of the original epoxy without clay.

Hua Ren, Jianzhong Sun, Binjie Wu and Qiyun Zhou [12], 2007, concerned in synthesis and properties of a phosphorus-containing flame retardant epoxy resin based on bis-phenoxy (3-hydroxy) phenyl phosphine oxide. A reactive phosphorus-

containing compound, bis-phenoxy (3-hydroxy) phenyl phosphine oxide (BPHPPO) was first successfully synthesized to produce the phosphorus-containing flame retardant epoxy resin (BPHPPO-EP). The chemical structures were characterized from FTIR, MS, NMR spectra and elemental analyses. Thermal degradation behaviors and flame retardant properties of the cured epoxy resins were investigated from the thermogravimetric analysis (TGA) and the limiting oxygen index (LOI) test using 4,4-diaminodiphenylsulfone (DDS) as curing agent. The high char yields and the high limiting oxygen index values were found to certify the great flame retardancy of this phosphorus-containing epoxy resin.

Hasmukh A. Patel, Rajesh S. Somani, Hari C. Bajaj, and Raksh V. Jasra [13], 2006, studied in preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. Quaternary phosphonium cations (hexadecyl tributyphosphonium; tetradecyl tributylphosphonium; tetraphenylphosphonium; methyl triphenylphosphonium; ethyl triphenylphosphonium and propyl triphenylphosphonium) were intercalated into montmorillonite (MMT) rich bentonite of Indian origin, by ion exchange reaction. The phosphonium MMT were characterized by Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction analysis (PXRD), particle size distribution (PSD) and thermogravimetric analysis (TGA). The phosphonium cations significantly influenced the particle size distribution. With longer alkyl chain finer particles were formed. The tetrabutylphosphonium and tetraphenylphosphonium MMT showed enhanced thermal stability (300–400 °C) and may be potentially useful materials for melt processing of polymer/layered silicates nanocomposites.

2.6 Poly(methyl methacrylate), PMMA [17]

Polymethyl methacrylate (PMMA) or poly(methyl 2-methylpropenoate) is a clear and colorless polymer, a kind of thermoplastic, by synthetic polymer of methyl methacrylate, used extensively for optical applications, such; lenses, light covers, glazing (particularly in aircraft), light pipes, meter covers, bathroom fittings, outdoor

signs, skylights, baths, toys. Acrylic film is laminated over ABS sheet to provide UV protection.

PMMA has some advantage properties, such as, excellent clarity and UV resistance, good abrasion resistance, hardness and stiffness, low water absorption, low smoke emission, good track and arc resistance. But it also has poor solvent resistance, low continuous used temperature of approx. 50°C, poor fatigue resistance, and notch sensitive properties.

PMMA has another advantage over glass. PMMA is more transparent than glass. When glass windows are made too thick, they become difficult to see through. But PMMA windows can be made as much as 13 inches (33 cm) thick, and they're still perfectly transparent. PMMA is also found in paint. Acrylic "latex" paints often contain PMMA suspended in water. PMMA doesn't dissolve in water, so dispersing PMMA in water requires we use another polymer to make water and PMMA compatible with each other. But PMMA is more than just plastic and paint.

But PMMA is more than just plastic and paint. Often lubricating oils and hydraulic fluids tend to get really viscous and even gummy when they get really cold. This is a real pain when you're trying to operate heavy equipment in really cold weather but when a little bit PMMA is dissolved in these oils and fluids, they don't get viscous in the cold, and machines can be operated down to -100 ^{o}C that is presuming the rest of the machine can take that kind of cold. PMMA is a vinyl polymer, made by free radical vinyl polymerization from the monomer methyl methacrylate.

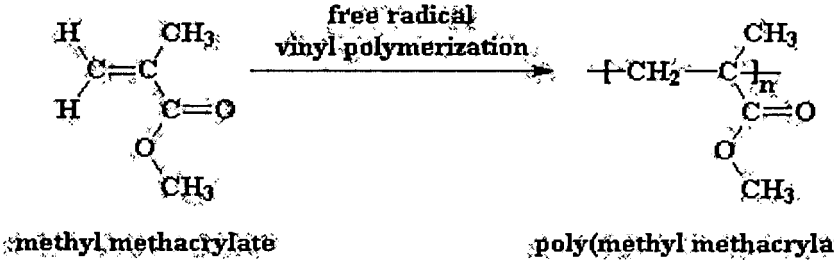


Fig.2.8 Polymerization of methyl methacrylate monomer via free radical vinyl polymerization

2.7 Related literature reviews

Tomohiro YAMAGUCHI, and Eisuke YAMADA, [14], 2006, concerned in preparation and properties of clay/SEBS intercalated composites. Clay/polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene triblock copolymer (SEBS) intercalated composites were prepared by melt-blending. The clays were a pristine montmorillonite (Mt) and three organically modified montmorillonites (organo-Mts) with different amounts of distearyldimethylammonium (D18) cation. The amounts of D18 were 50, 70 and 100% of the cation exchange capacity (denoted as D18Mt(50), D18Mt(70) and D18Mt(100), respectively). The clay/SEBS composites were characterized by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction analysis (XRD). The dynamic mechanical analysis (DMA) and the tensile properties were also examined.

The size of agglomerated clay particles decreased with the increasing amount of D18. The FE-SEM image of D18Mt(100)/SEBS revealed that the clay particles were dispersed at the sub-m m level (100–500 nm). The XRD patterns suggested that the SEBS chains were inserted into the interlayers of the organo-Mts. The DMA curves indicated that the addition of the organo-Mts produced an increase in the storage modulus in the rubbery plateau region, but a slight decrease in the glass transition temperature of the polystyrene domains. The tensile properties of the organo-Mt/SEBS composites were higher than those of the unmodified Mt/SEBS. D18Mt(100)/SEBS displayed an improved tensile modulus, tear strength and

hardness compared to pure SEBS, without sacrificing the tensile strength and elongation at break.

S I Marras, A Tsimpliaraki, I Zuburtikudis and C Panayiotou, [15], 2007, studied on surfactant-induced morphology and thermal behavior of polymer layered silicate nanocomposites. Poly(L-lactic acid) nanocomposites were prepared by the addition of montmorillonite modified with various loadings of hexadecylammonium cation. The influence of alkylammonium on the morphology and surface charge of the clay was investigated by Xray diffraction (XRD) analysis and electrokinetic measurements, respectively. The structural characteristics of the inorganic-organic hybrids were studied by XRD, transmission electron microscopy (TEM) and atomic force microscopy (AFM). Thermal analysis was carried out by thermogravimetric analysis (TGA) under constant nitrogen flow and under air. The results showed that high concentration of surfactant present in the clay greatly increases clay's dispersibility into the matrix and this substantially improves the thermal stability of the pristine polymer.

Christine M. Moore, Sarah Hackman, Terrance Brennan and Shelley D. Minteer, [16], 2005, concerned in effect of mixture casting phosphonium salts with Nafion® on the proton exchange capacity and mass transport through the membranes. This research examined how the physical properties of Nafion® were affected by mixture casting Nafion® with quaternary phosphonium salts. Quaternary phosphonium salts could be mixture cast with commercially available Nafion® suspension to form membranes with decreased proton exchange capacity and altered mass transport of cations, anions and neutral species through the membrane. Since quaternary phosphonium salts were similar in size and hydrophobicity to quaternary ammonium salts, the mass transport of cations, anions and neutral species through tetraethylphosphonium bromide and tetrabutylphosphonium treated Nafion® was similar to tetraethylammonium bromide and tetrabutylammonium treated Nafion®, respectively. Although there was no statistically significant difference between transports through tetrabutylphosphonium bromide treated Nafion® membranes and tetrabutylammonium bromide treated Nafion® membranes, there was a detectable

difference for the transport of ferricyanide, methyl viologen and tetramethylphenylenediamine through tetraethylphosphonium bromide treated Nafion® membranes. The difference was consistent with the fact that tetraalkylphosphonium bromides were slightly larger than tetraalkylammonium bromides, so the resulting pore size for a tetraalkylphosphonium bromide treated Nafion® membrane was larger than the pore size for a tetraalkylammonium bromide treated Nafion® membrane. The proton exchange capacity of tetraalkylphosphonium bromide treated membranes was larger than tetraalkylammonium bromide treated membranes. This data was expected since phosphonium salts were less hydrophobic than the ammonium salts and would have a lower affinity for the sulfonic acid exchange sites. Overall, this research indicates that quaternary phosphonium bromide salts could be employed to further tailor the physical and chemical properties of Nafion® membranes.

Chapter 3

Experimental Details

3.1 Materials

3.1.1 Mac-gel Montmorillonite (MMT), Thai Nippon.

3.1.2 Tetrabutylphosphonium bromide ($C_{16}H_{36}PBr$), Fluka, Analytical grade

3.1.3 Methyl methacrylate monomer ($C_5H_8O_2$, Molecular weight = 100.12, Density = 0.963 g/ml), Aldrich, Analytical grade

3.1.4 Sodium hydroxide (NaOH), LAB scan, Analytical grade

3.1.5 Sodium chloride (NaCl), CARLO ERBA, Analytical grade

3.1.6 Anhydrous sodiumsulphate (Na_2SO_4), CARLO ERBA, Analytical grade

3.1.7 Benzoyl peroxide (BPO), CARLO ERBA, Analytical grade

3.1.8 Methanol (CH_3OH), Fisher, Commercial grade

3.1.9 Toluene (C_7H_8), LAB SCAN, Analytical grade

3.1.10 Dichloromethane (CH_2Cl_2), Fisher, Analytical grade

3.1.11 Xylene (C_8H_{10}), Fisher, Analytical grade

3.1.12 Silver nitrate ($AgNO_3$) 0.1%

3.1.13 Nitrogen gas (N_2)

3.1.14 Distilled water

3.2 Apparatus

3.2.1 Glasswares

3.2.2 Balance, TC-254, Denver Instrument

3.2.3 Peristaltic pump, V 77120-52, Cole Parmer

3.2.4 Ultrasonic bath, ULTRAsonik, Fisher Scientific Worldwide

3.2.5 Mechanical stirrer with turbine, EURO-ST B, IKA LABORTECHNIK STAUFEN

3.2.6 Water bath

3.2.7 Desiccator

3.2.8 Oven

3.2.9 Vacuum filter

3.2.10 Magnetic bar

3.2.11 glass substrate

3.2.12 Micrometer

3.2.13 Mortar and pestle

3.2.14 Litmus paper

3.2.15 Sieve 400 mesh

3.2.16 X-ray diffractometer (XRD), D8 Advance, Bruker AG

3.2.17 X-ray fluorescence spectrometer (XRF), SRS 3400, Bruker AG

3.2.18 Thermogravimetric analyser (TGA), Pyris 1 TGA, Perkin Elmer

3.2.19 UV-Visible Spectrometer (UV-vis), He λ ions α, Thermo Electron Corporation

3.2.20 Gel permeation chromatographer (GPC), Water 150-CV, Milipore

3.3 Preparation of the Organoclays

3.3.1 Preparation of swelled montmorillonite (S-MMT)

1. 25.0 g of sodium montmorillonite (Na^+-MMT) was added into 3000 ml of distilled water.

2. The mixture was sonicated for 2 hours in order to separate the montmorillonite tactoids.

3. The S-MMT was dried in the oven at 100 °C for 48 hours.

4. The S-MMT was ground with mortar.

3.3.2 Preparation of tetrabutylphosphonium bromide solution

- 0.72 g of tetrabutylphosphonium bromide (TBPB) was dissolved into 10 ml distilled water *(0.21 M)*.

3.3.3 Preparation of modified MMT (P-MMT)

1. 2.0 g of S-MMT was added into 600 ml of distilled water.

2. The mixture was sonicated for 1 hour.

3. 0.21 M TBPB solution was slowly added by using peristaltic pump with sonication for 1 hour.

4. P-MMT mixture was filtered by using vacuum filter and it was rinsed several times with distilled water until the testing of the mother liquor with 0.1 mol/L of $AgNO_3$ showed the clear solution, having no white precipitate formation.

5. P-MMT cake was dried in an oven at 110 °C for 48 hours.

6. P-MMT was ground with mortar, and then sieved with the sieve 400 mesh.

7. P-MMT was characterized by using XRD, XRF and TGA techniques.

8 All steps were repeated by using mechanical stirrer instead of sonication in the 3rd step.

3.4 Synthesis of Poly(methyl methacrylate), PMMA

3.4.1 Extraction of inhibitor from MMA monomer

1. 10 ml of MMA and 10 ml of 10% NaOH solution were mixed well in separatory funnel.

2. The mixture was lead until completely separation into 2 phases.

3. The NaOH phase was removed (bottom phase).

4. Another 10 ml of 10% NaOH solution was added into the separatory funnel and the 1st-3rd step were repeated.

5. Deinhibitor-MMA was washed with distilled water for several times until the litmus paper had no changed from red to blue.

6. 10 ml of saturated NaCl solution was added and extracted the lower phase for twice times.

7. Anhydrous sodium sulfate was added into MMA phase to remove water.

8. The solid phase of anhydrous sodium sulfate was separated by gravimetric filtration and the liquid phase (fresh MMA) was collected and kept in the refrigerator.

3.4.2 Synthesis of PMMA by solution polymerization

1. 10 ml of fresh MMA and 0.01 g of benzoyl peroxide (BPO) were dissolved in 40 ml of toluene.

2. The solution was purged with nitrogen gas for 15 minutes, then capped with equipment connecting with the filled nitrogen gas balloon and wrapped with paraffin film.

3. The solution was heated in water bath at 85 °C for 24 hours. After that, the solution was let to cool down at room temperature.

4. The white solid of PMMA was precipitated by dropping wise the solution into the well stirring of 600 ml methanol.

5. The solid was dried in an oven at 60 °C for 2 hours.

6. Molecular weight of PMMA was calculated by GPC technique.

3.5 Solvent Screening of PMMA, and P-MMT

3.5.1 Solubility of PMMA

1. PMMA was dissolved in the solvents, i.e., dichloromethane, xylene, and toluene with ratio of solid: liquid 1%w/v.
2. The mixtures were sonicated for 30 minutes.
3. The solubility of PMMA mixtures was observed. If it necessary, the mixtures might be further sonicated at 60 °C for 30 minutes to increase the solubility of PMMA.
4. The good solvent for PMMA was chosen.

3.5.2 Dispersion and swelling of P-MMT

1. P-MMT was dispersed in the solvents, i.e., dichloromethane, xylene, and toluene at the ratio of 1%w/v.
2. Each mixture was sonicated for 30 minutes.
3. The dispersion and the swelling of P-MMT were observed and chosen the best condition mixture that P-MMT could be dispersed for the longest time with good swelling.

3.6 Preparation of PMMA/P-MMT film by Spin on Glass Substrate

1. 0.07 g of P-MMT was dispersed in 10 ml of toluene by using sonication technique for 30 minutes. …….. (Mixture no.1)

2. 7.0 g of PMMA was slowly dissolved in 20 ml of toluene by using magnetic stirrer. …….. (Mixture no.2)

3. Mixture no.2 was mixed into mixture no.1, and then, PMMA/P-MMT solution was stirred continuously until PMMA was completely dissolved.

4. PMMA/P-MMT solution was coated on a glass substrate by using spin technique at speed 180 rpm to get PMMA/P-MMT film.

5. PMMA/P-MMT films were characterization by using XRD, TGA and UV/VIS/NIR spectrometer.

6. All steps were repeated by increasing the weight of P-MMT to be 0.14 g, 0.21 g and 0.42 g, respectively.

(ratio of P-MMT in PMMA; 1%, 2%, 3% and 6%)*

3.7 Characterization of TBPB, S-MMT, P-MMT, PMMA and PMMA/P-MMT films

3.7.1 X-ray Diffractometer (XRD)

X-ray diffraction pattern and data were recorded using Cu K_α radiation (λ = 15.4 nm) at a voltage of 30 kV and a current of 30 mA (scanning condition: 2θ 1-25 degree, step size 0.04 degree, and time/step 0.50 sec). S-MMT, P-MMT, PMMA and PMMA/P-MMT films were characterized by using this technique.

3.7.2 X-ray Fluorescence (XRF)

P-MMT sample (0.50 g) was mixed with boric acid (4.50 g), ground by bench mill (A 1, Rock labs) for 1 min, and then compressed to pellet by uniaxial pressing. The chemical composition of the samples was determined by X-ray Fluorescence Spectrometry.

3.7.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of TBPB, S-MMT, P-MMT, and PMMA/P-MMT films was performed by using thermogravimetric analyzer. This technique was used to determine the TBPB content in P-MMT and PMMA/P-MMT films, and the decomposition temperature of compounds. TGA was performed in the temperature range of 50–700 °C at the heating rate of 10 °C/min under the air and nitrogen conditions (flow rate of 40 cm^3/min).

3.7.4 UV-vis Spectrometer

UV absorbance and percentage of transmittion (%T) of PMMA/P-MMT films were determined by using UV-vis spectrometer in scanning mode at wavelength between 200-1000 nm.

3.7.5 Gel Permeation Chromatographer (GPC)

Molecular weight of PMMA was calculated by using this technique with the following testing condition;

Column set	: PL GEL 10 μm Mixed B 2 columns
	Size 7.8 x 300.0 μm
	(MW resolving range = 500-10,000,000)
Eluent	: Tetrahydrofuran (THF)
Polymer standard	: Polystyrene (PS)
Column temperature	: 30 °C
Injector temperature	: 30 °C
Solvent/pump temperature	: 30 °C
Flow rate	: 1.0 ml/min

Injection volume	: 100.00 µl
Analysis time	: 22 min
Detector	: Refractive index
Sample preparation	: Dissolved with THF
Calibration method	: Polystyrene standard calibration (MW 4,490-1,112,000)

Chapter 4
Results and Discussion

4.1 Characterization of MMT and P-MMT

4.1.1 X-ray Diffractometer (XRD)

The XRD patterns of fresh sodium montmorillonite (Na^+-MMT), swelled montmorillonite (S-MMT), P-MMT modified by using mechanical agitation (P-MMT_Mech), and P-MMT modified by using sonication technique (P-MMT_Sonic) were showed in Fig. 4.1. When clay was swelled with deionized water, the peak of clay shifted from $2\Theta = 6.12°$ ($d_{001} = 1.44$ nm) to be the peak of MMT at $2\Theta = 7.24°$ ($d_{001} = 1.22$ nm). The smaller d-spacing of clay indicated the cation exchange occurred between proton (H^+) of deionized water and exchangeable ions, mainly Na^+ ions.

From the XRD patterns of P-MMT_Mech and P-MMT_Sonic, the d_{001} peak shifted from the peak of S-MMT at $2\Theta = 7.24°$ ($d_{001} = 1.22$ nm) to $2\Theta = 5.64°$ ($d_{001} = 1.57$ nm) and $2\Theta = 5.56°$ ($d_{001} = 1.59$ nm), respectively. The d-spacing of P-MMT was wider than that of S-MMT, indicating the intercalation of phosphonium ions into the layers of montmorillonite, as shown in Fig. 4.2 (a) and (b).

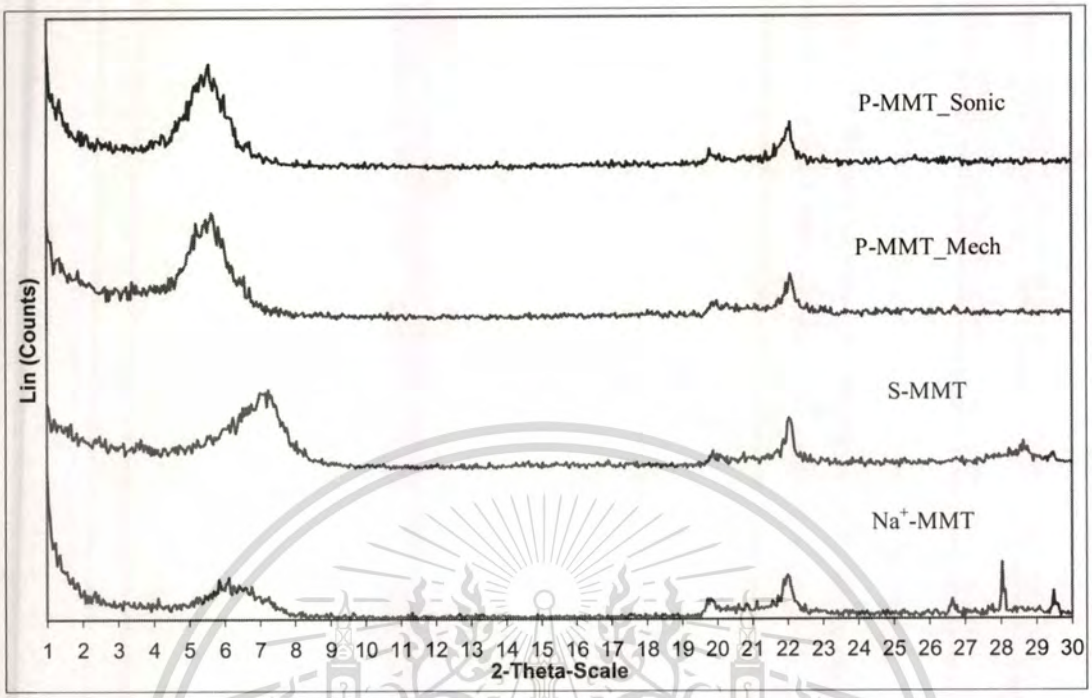
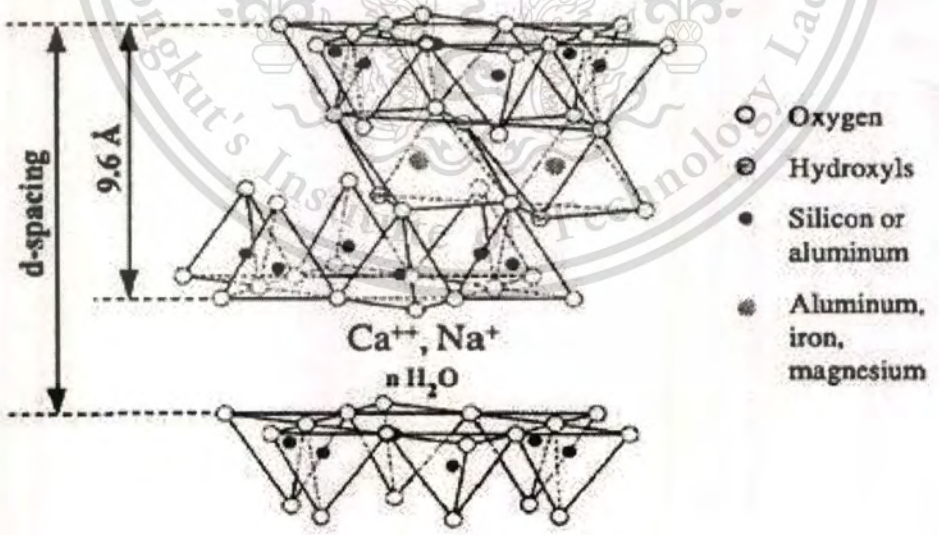


Fig. 4.1 XRD patterns of Na^{+}-MMT, S-MMT, P-MMT_Mech and P-MMT_Sonic



(a)

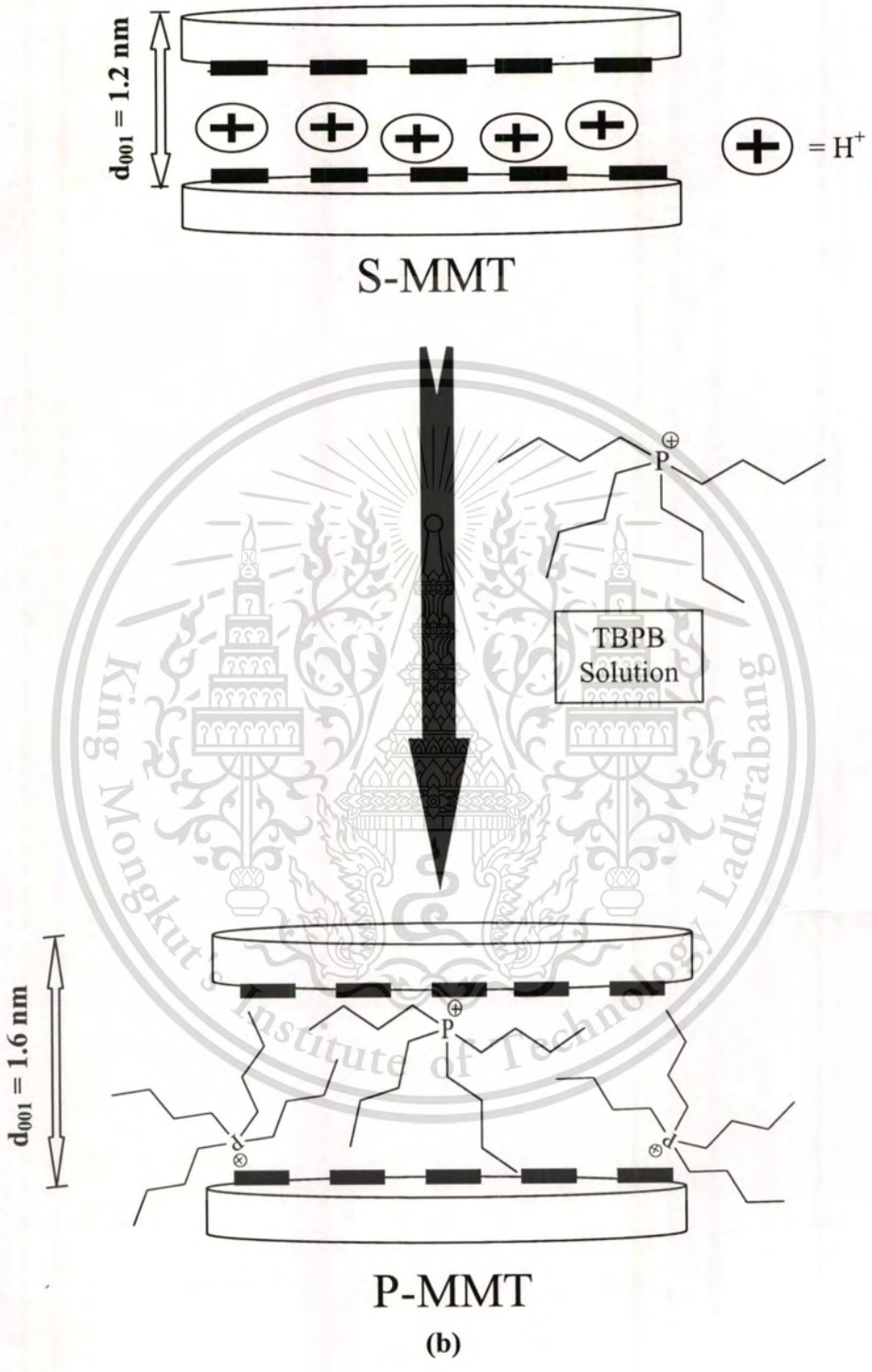


Fig. 4.2 (a) Crystalline structure of montmorillonite and (b) Schematic of TBPB intercalated with S-MMT

4.1.2 X-ray Fluorescence (XRF)

The chemical composition of S-MMT and P-MMT were shown in Appendix A. The molar ratios of Na:Al, Si:Al and P:Si were calculated and concluded in Table 4.1. The Na content could be determined in the S-MMT, corresponding to the Na^+ counter ion between clay layers. The Na^+ ions could exchange with phosphonium ions of TBPB, which could be the P content in P-MMT. If they completely exchanged, the Na content should not be detected in P-MMT. This result has corroborated to the intercalation of phosphonium ions into the MMT layers.

Table 4.1 The molar ratio of Na:Al, Si:Al and P:Si of S-MMT and P-MMT

Entry	Sample	Na:Al	Si:Al	P:Si
1	S-MMT	0.24	3.50	-
2	P-MMT_Mech	-	3.63	0.04
3	P-MMT_Sonic	-	3.74	0.04

4.1.3 Thermogravimetric Analysis (TGA)

The degradation temperature and percentage of weight loss of the S-MMT, tetrabutylphosphonium bromide (TBPB) and P-MMT were investigated by TGA under oxygen atmosphere. Fig.4.2 - 4.5 show the thermograms of the S-MMT, TBPB, P-MMT_Mech and P-MMT_Sonic, respectively.

From the thermogram of S-MMT (Fig. 4.2) shows a long range of degradation period (60 - 680 °C) with the weight loss about 11% by weight that could be divided into 2 main regions. The first degradation (60 - 100 °C) region was due to the moisture content with the weight loss of about 7% by weight. The second region was the degradation of the organic impurities in natural clay (580 -680 °C), their weight was loosed about 4.3% by weight. For the TBPB (Fig. 4.3), it was shown the degradation period between 120 - 600 °C, due to the decomposition of TBPB. For the decomposition of P-MMT (Fig. 4.4 and 4.5) was observed in the temperature range of 140 – 700 °C, corresponding to the decomposition of TBPB and organic matter in the S-MMT.

Table 4.2 Amount of TBPB intercalated in MMT layers.

Sample	Starting degradation temperature of organic phase (^{o}C)	Complete degradation temperature of organic phase (^{o}C)	Amount TBPB in P-MMT (wt %)
S-MMT	60	680	-
TBPB	120	600	-
P-MMT_Mech	140	700	5.39
P-MMT_Sonic	140	700	5.89

According to the Table 4.2, the degradation temperature of intercalated TBPB was higher than raw TBPB for 20 ^{o}C due to the interaction between phosphonium ions and MMT surface. From the composition data from XRF and %weight loss in Table 4.2, the TBPB could be intercalated in MMT layers by using both mechanical stirrer and sonication because the characterization results have not shown the significance different in amount of intercalated TBPB.

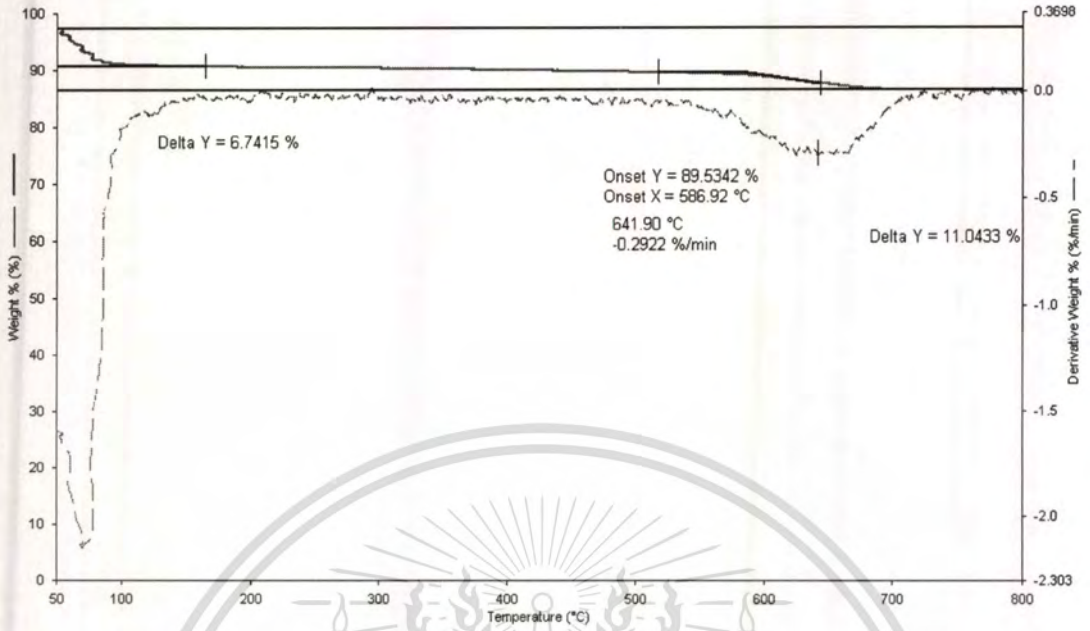


Fig. 4.3 Thermogram of S-MMT

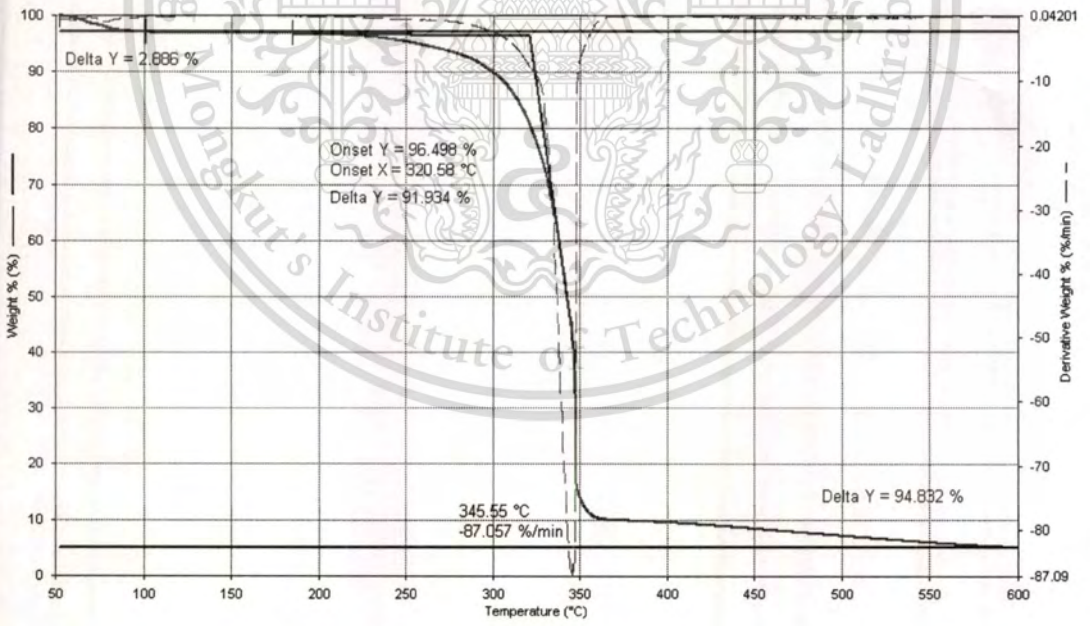


Fig. 4.4 Thermogram of tetrabutylphosphonium bromine

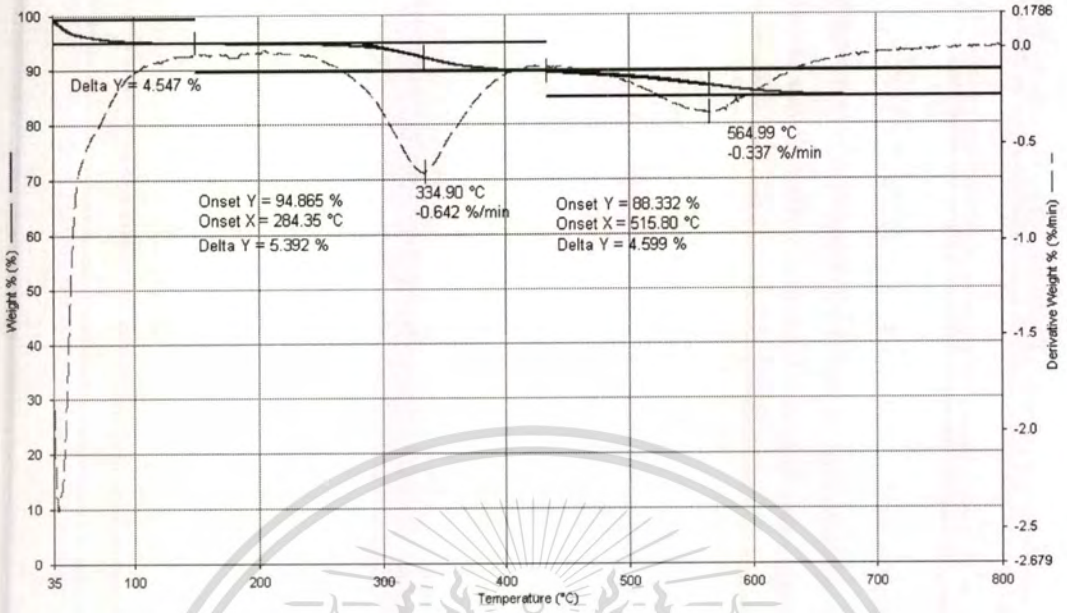


Fig. 4.5 Thermogram of P-MMT_Mech

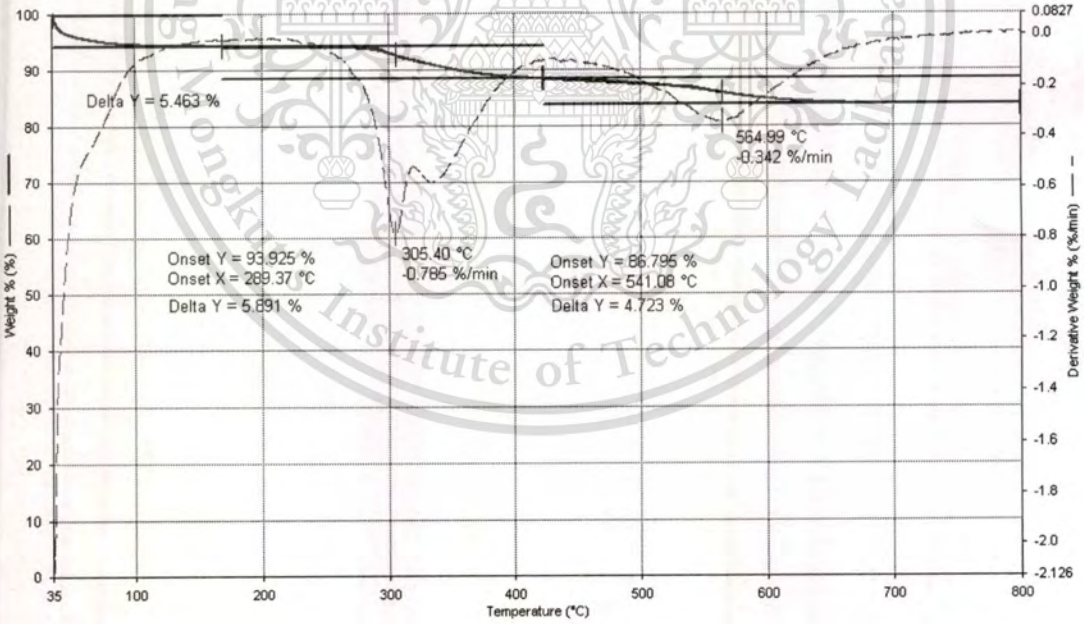


Fig. 4.6 Thermogram of P-MMT_Sonic

4.2 Synthesis of PMMA by solution polymerization

4.2.1 Gel Permeation Chromatographer (GPC)

PMMA, which was synthesized by using solution polymerization method, has the percentage of productivity in the range of 47-57 %. Their molecular weight was determined by GPC technique. The results were found that $\overline{M}_n$ = 61,312 g/mole, $\overline{M}_w$ = 123,461 g/mole and MWD = 2.01.

4.3 Solvent Screening of PMMA and P-MMT

The outcome of this investigation was shown in Fig. 4.6. The P-MMT could be swelled and dispersed for the longest period in toluene. For PMMA, it could be dissolved with all in this set of solvents homogeneously. Hence, toluene would be used as the solvent for preparation of PMMA/P-MMT film.

(a) **(b)** **(c)**

Fig. 4.7 Dispersion and swelling of P-MMT in various solvents; (a) dichloromethane, (b) xylene and (c) toluene at the ratio of 1%w/v *(This picture was taken after one week left)*

4.4 Characterization of PMMA/P-MMT films

4.4.1 X-ray Diffractometer (XRD)

Fig. 4.7 shows the XRD patterns of P-MMT_Mech and PMMA/P-MMT films. The characteristic peak of P-MMT could not be observed in the XRD patterns of composite films, indicating that the tactoid of P-MMT was destroyed by penetrating of PMMA into the 001 plane of MMT layers. These results represented the exfoliation of MMT tactoids in the PMMA/P-MMT film. In addition, the present of P-MMT in nanocomposite films was characterized by XRF and TGA as shown in the Appendix-A, Appendix-B and Appendix-C.

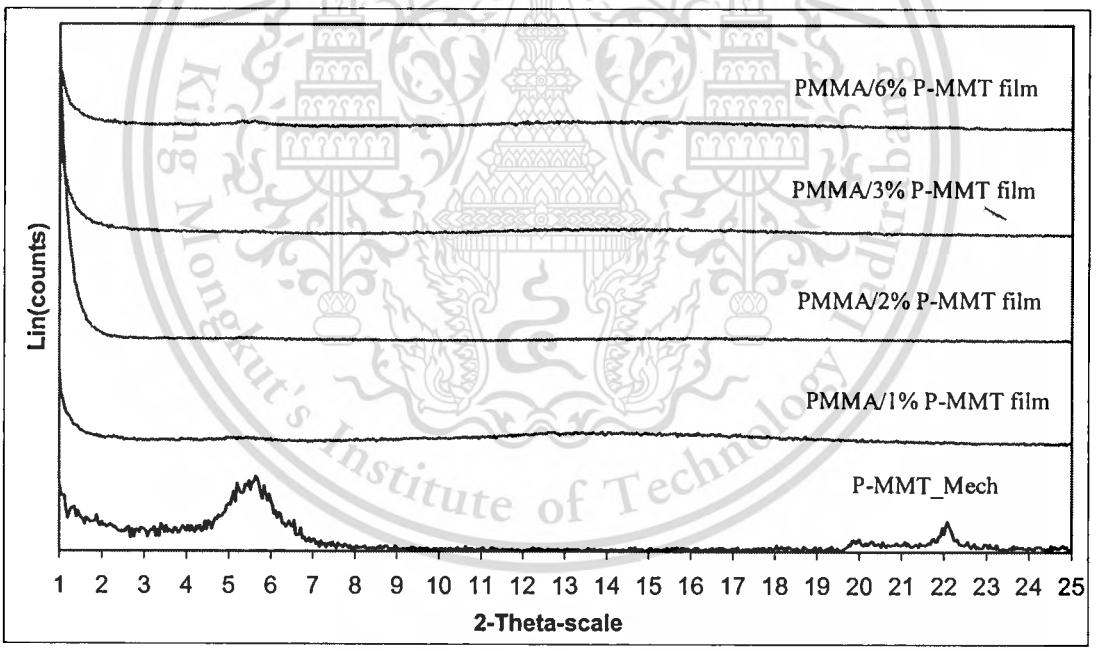


Fig. 4.8 The XRD patterns of P-MMT_Mech and PMMA/P-MMT films

4.4.2 Thermogravimetric Analysis (TGA)

PMMA film and PMMA/P-MMT films were characterized by TGA under both of oxygen and nitrogen atmospheres. From Fig. 4.8 and the decomposition temperature of PMMA and PMMA/P-MMT films under oxygen atmosphere in Table 4.3, they were seen that starting decomposition temperature of films increased slightly with higher concentration of P-MMT. The reason for this case was supposed that P-MMT has flat shape and well dispersion in the films, so that the oxygen molecules could not directly interact with PMMA molecules to get the combustion. Therefore, the combustion between PMMA and oxygen was interfered by P-MMT filling, at this point; P-MMT could be regarded as an oxygen barrier. However, the starting decomposition temperature of films was found to be lower at 6% P-MMT filling because P-MMT might start to agglomerate, that decreased amount of oxygen barrier.

The complete decomposition temperature of PMMA was slightly increased with higher amount of P-MMT; this was indicated in Fig. 4.9 and the decomposition temperature of PMMA and PMMA/P-MMT films under nitrogen atmosphere in Table 4.4. In this case, the well dispersed P-MMT might be acting as an insulator, which could delay the heat transfer from hot N_2 gas by absorbing and spreading heat on their surface. The increment of the complete decomposition temperature of PMMA might be concerned that the heat stability of PMMA was improved with P-MMT filling.

Table 4.3 Decomposition temperature of PMMA and PMMA/P-MMT films under oxygen atmosphere

Sample	Starting decomposition temperature (°C)	Complete decomposition temperature (°C)	Total weight loss (wt %)
PMMA	258	365	98.95
PMMA/1% P-MMT film	263	360	98.60
PMMA/2% P-MMT film	263	365	97.85
PMMA/3% P-MMT film	265	370	96.07
PMMA/6% P-MMT film	261	370	94.17

Table 4.4 Decomposition temperature of PMMA and PMMA/P-MMT films under nitrogen atmosphere

Sample	Starting decomposition temperature (°C)	Complete decomposition temperature (°C)	Total weight loss (wt %)
PMMA	223	407	99.43
PMMA/1% P-MMT film	212	406	98.22
PMMA/2% P-MMT film	224	403	97.76
PMMA/3% P-MMT film	224	413	97.01
PMMA/6% P-MMT film	230	416	94.97

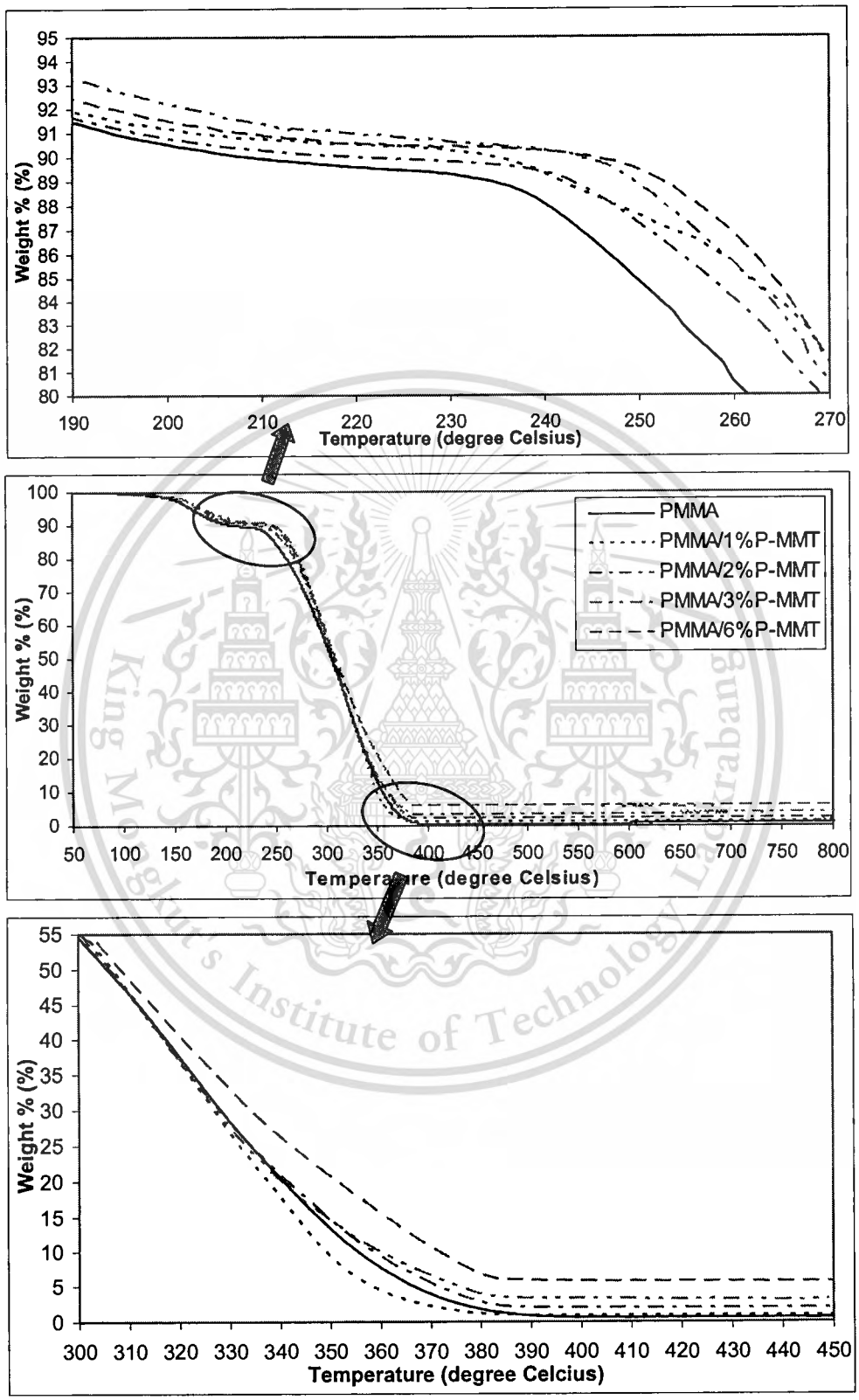


Fig. 4.9 Thermogram of PMMA film and PMMA/P-MMT films under oxygen atmosphere

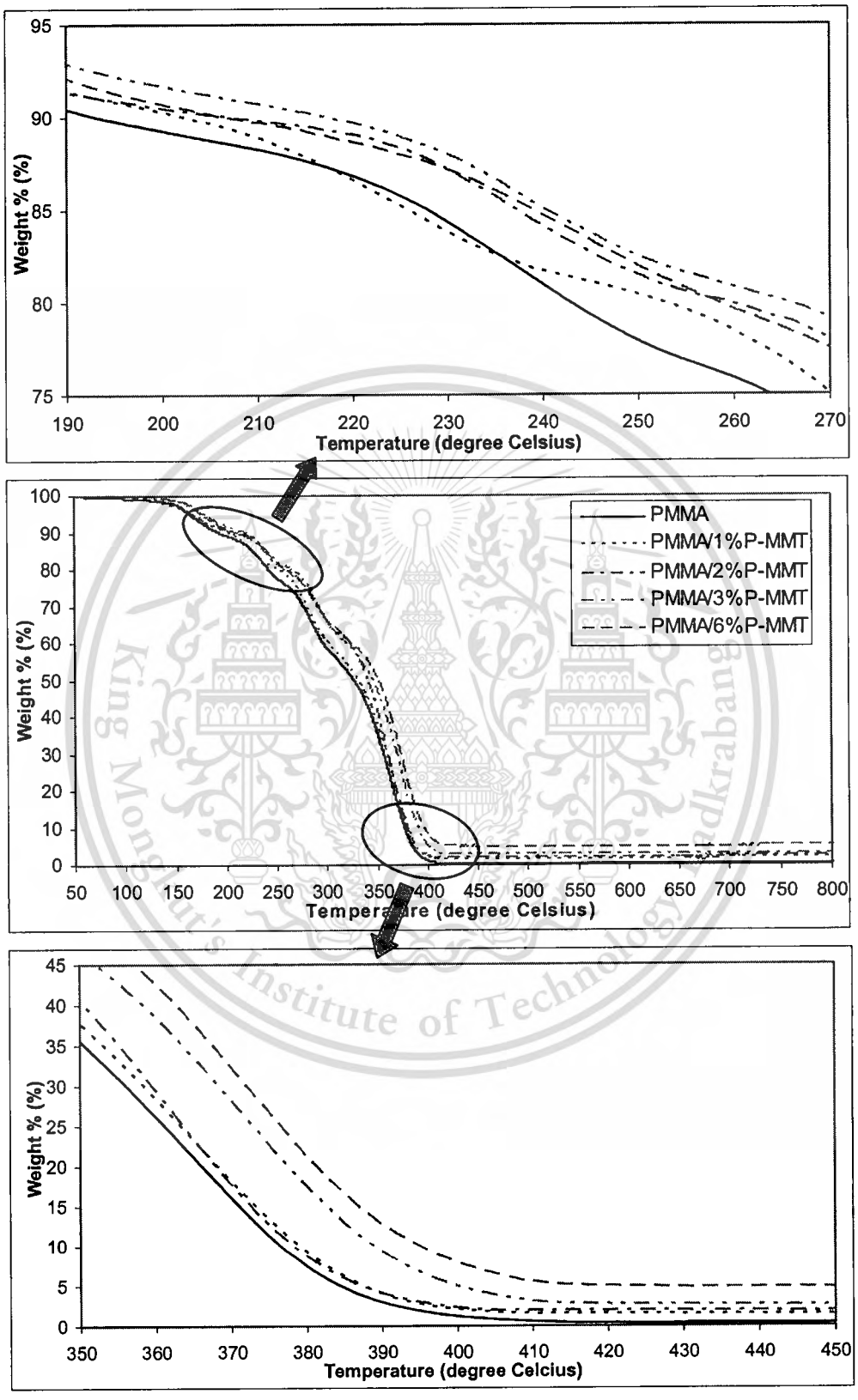


Fig. 4.10 Thermogram of PMMA film and PMMA/P-MMT films under nitrogen atmosphere

4.4.3 UV-vis Spectrometer

The percentage of transmittance of UV (190-400 nm) and visible light (400-600 nm) of PMMA and PMMA/P-MMT films were measured. Fig. 4.10 shows the UV-visible spectra of PMMA and PMMA/P-MMT films.

From Fig. 4.10, it was seen that the %transmittance decreased when the amount of P-MMT was increased. As if, the absorbance of these nanocomposite films was focused, it was found that their absorbance was higher in UV range, especially UV-A and UV-B, than those in the visible light region.

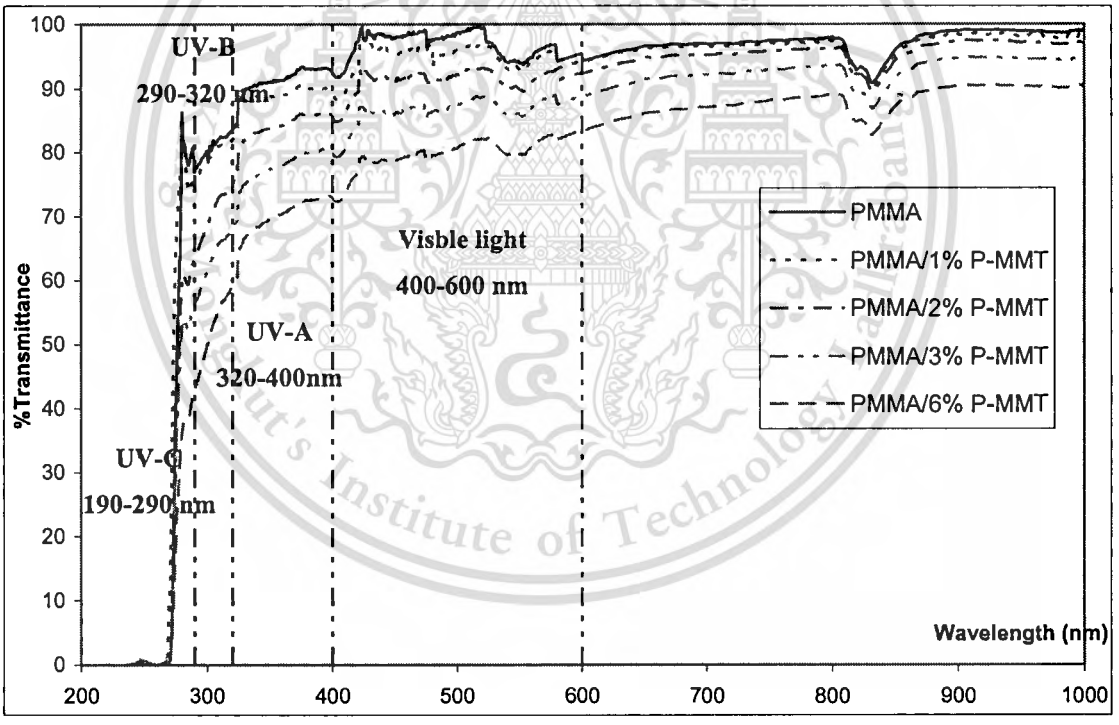


Fig. 4.11 UV-visible spectra of PMMA and PMMA/P-MMT films

Chapter 5
Conclusion and Recommendations

5.1 Conclusion

- Mechanical agitation and sonication techniques could be used for modification of montmorillonite by intercalation with tetrabutylphosphonium bromide. The amount of intercalated TBPB in the MMT was about 5.6 wt%. The degradation temperature of intercalated TBPB was higher than raw TBPB for 20 °C due to the interaction between phosphonium ions and MMT surface.

- The PMMA/P-MMT nanocomposite films containing 1, 2, 3 and 6 wt% P-MMT could be prepared by solvent casting technique. The heat stability was improved due to the action of exfoliated P-MMT.

- The absorbance of PMMA/P-MMT film was high in the UV region, especially in UV-A and UV-B, suggesting the potential to be used as the UV-screening film for the windscreen and the glasses lens.

5.2 Recommendations

1. TBPB might be replaced by the other cationic salts, which have higher heat stability or better properties.

2. The nanocomposite films containing P-MMT can be prepared from other kinds of polymers, which have same polarity as P-MMT.

3. The preparation condition of PMMA/P-MMT nanocomposite films should be modified in order to increase the P-MMT loading in the nanocomposite film, such as, using in situ polymerization technique.

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Appendix-A

XRF Results

Table A-1 Composition of P-MMT_Mech

Elements	%Atom (%)
O	49.8
Mg	2.42
Al	8.56
Si	32.2
P	1.44
Ca	1.45
Fe	1.75
K	0.778

Table A-2 Composition of P-MMT_Sonic

Elements	%Atom (%)
O	50.1
Mg	2.55
Al	8.45
Si	32.8
P	1.45
Ca	1.39
Fe	1.79
K	0.782

Table A-3 Composition of PMMA/1% P-MMT film

Elements	%Atom (%)
O	44.5
Na	3.15
Mg	2.29
Al	4.25
Si	28.7
P	1.82
Cl	3.11
K	1.99
Ca	2.11
Fe	2.06
Cu	2.21
Pd	1.29

Table A-4 Composition of PMMA/2% P-MMT film

Elements	%Atom (%)
O	42.8
Mg	1.66
Al	4.69
Si	26.7
P	1.88
Cl	2.88
K	2.34
Ca	4.89
Fe	3.69
Cu	3.03
Pd	1.81

Table A-5 Composition of PMMA/3% P-MMT film

Elements	%Atom (%)
O	44.5
Na	1.41
Mg	1.62
Al	4.84
Si	27.8
P	2.34
Cl	2.73
K	3.94
Ca	3.13
Fe	2.11
Cu	1.72

Table A-6 Composite of PMMA/6% P-MMT film

Elements	%Atom (%)
O	48.8
Na	0.915
Mg	1.49
Al	5.6
Si	31.6
P	2.7
K	1.69
Ca	2.91
Fe	2.12
Cu	0.83

Appendix-B

Thermogram of PMMA and PMMA/P-MMT films under oxygen atmosphere

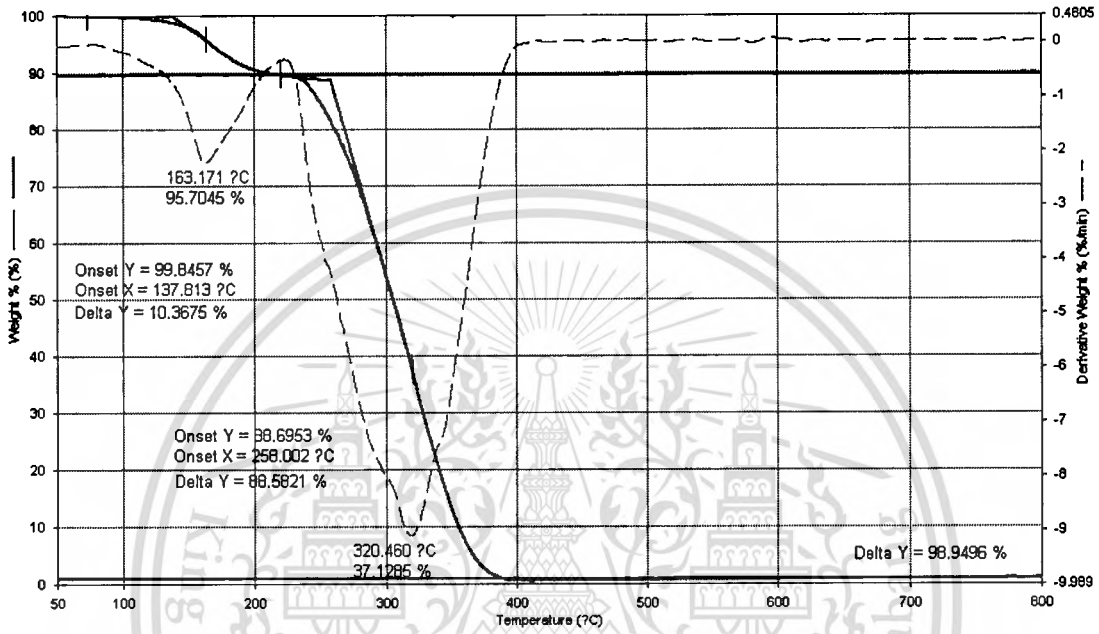

Fig. B-1 Thermogram of PMMA film

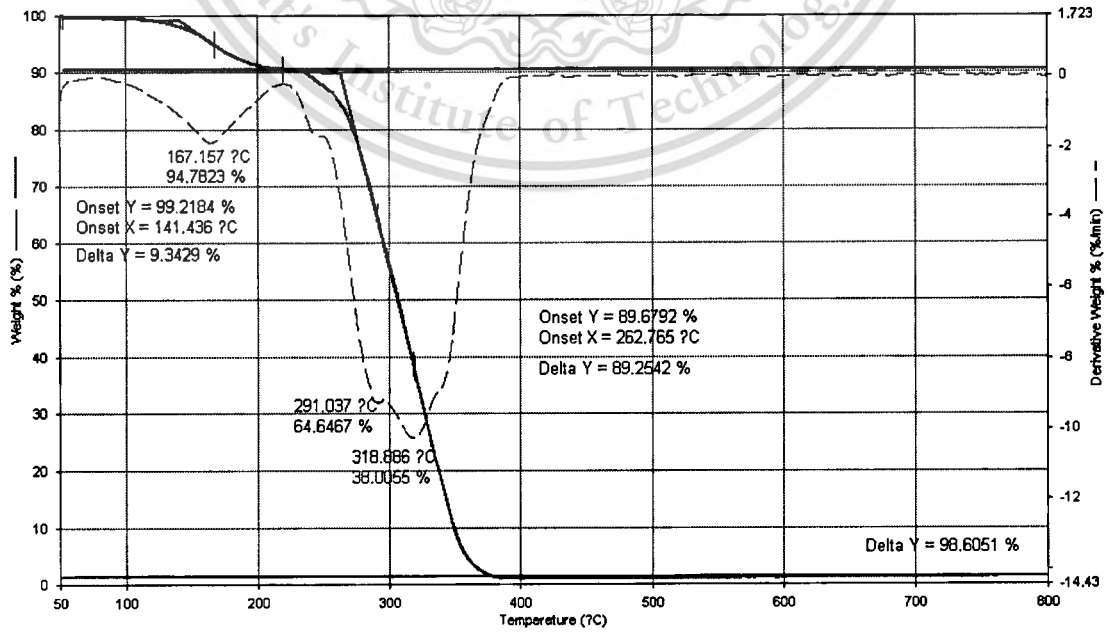

Fig. B-2 Thermogram of PMMA/1% P-MMT film

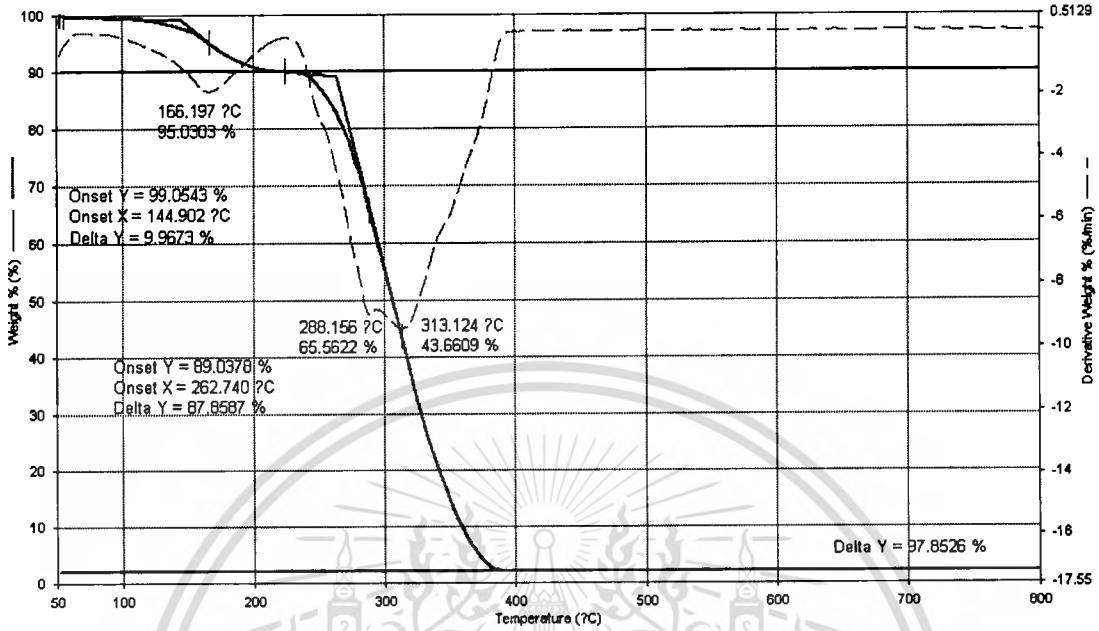

Fig. B-3 Thermogram of PMMA/2% P-MMT film

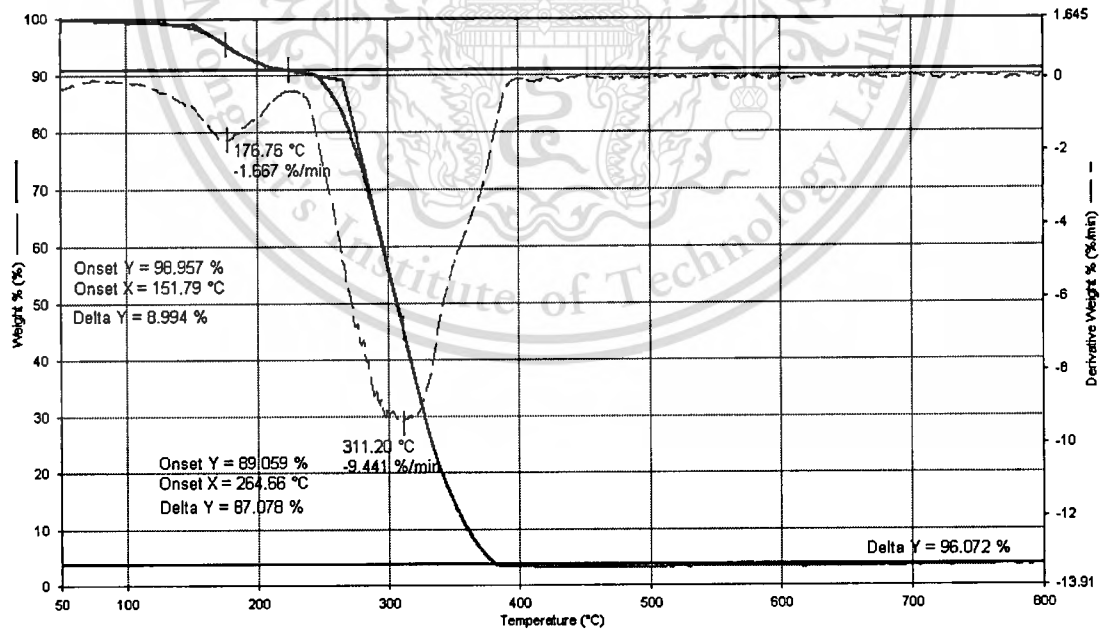

Fig. B-4 Thermogram of PMMA/3% P-MMT film

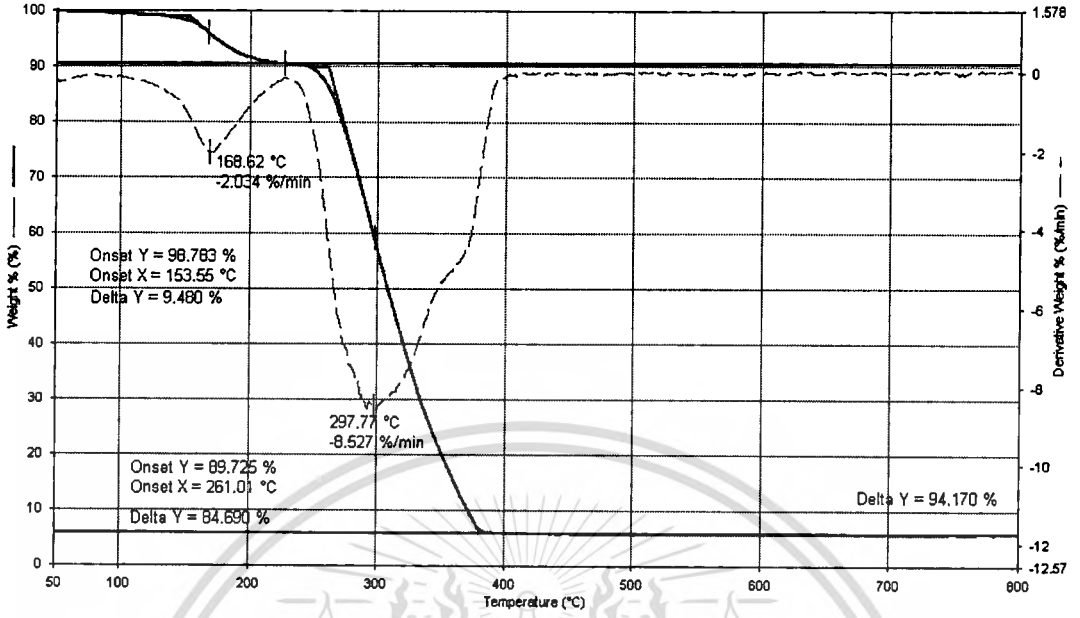

Fig. B-5 Thermogram of PMMA/6% P-MMT film

Appendix-C

Thermogram of PMMA and PMMA/P-MMT films under nitrogen atmosphere

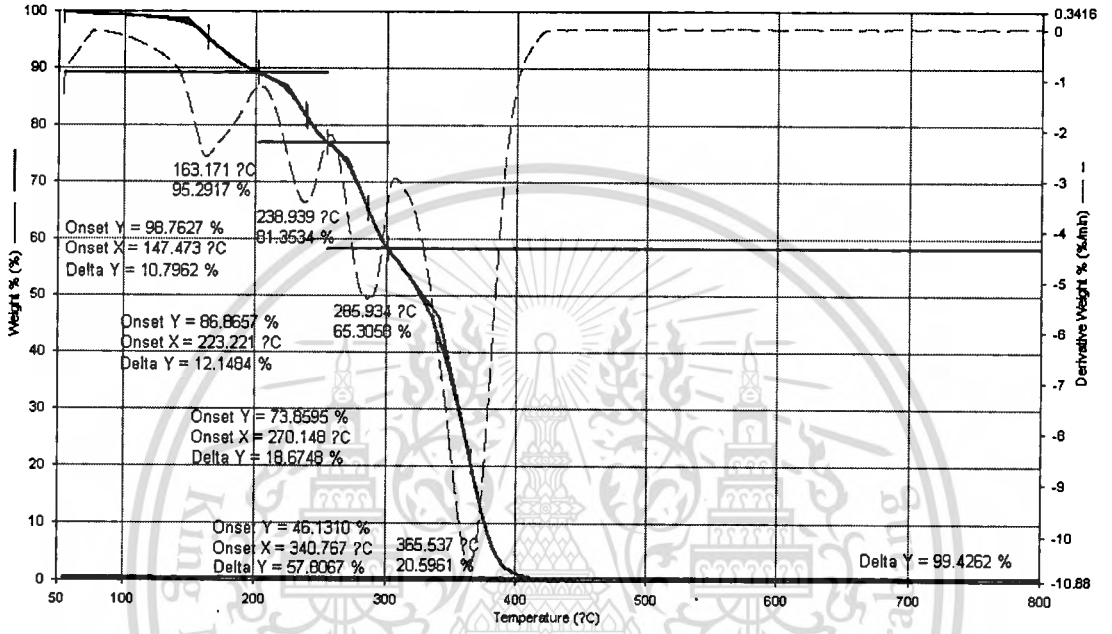

Fig. C-1 Thermogram of PMMA film

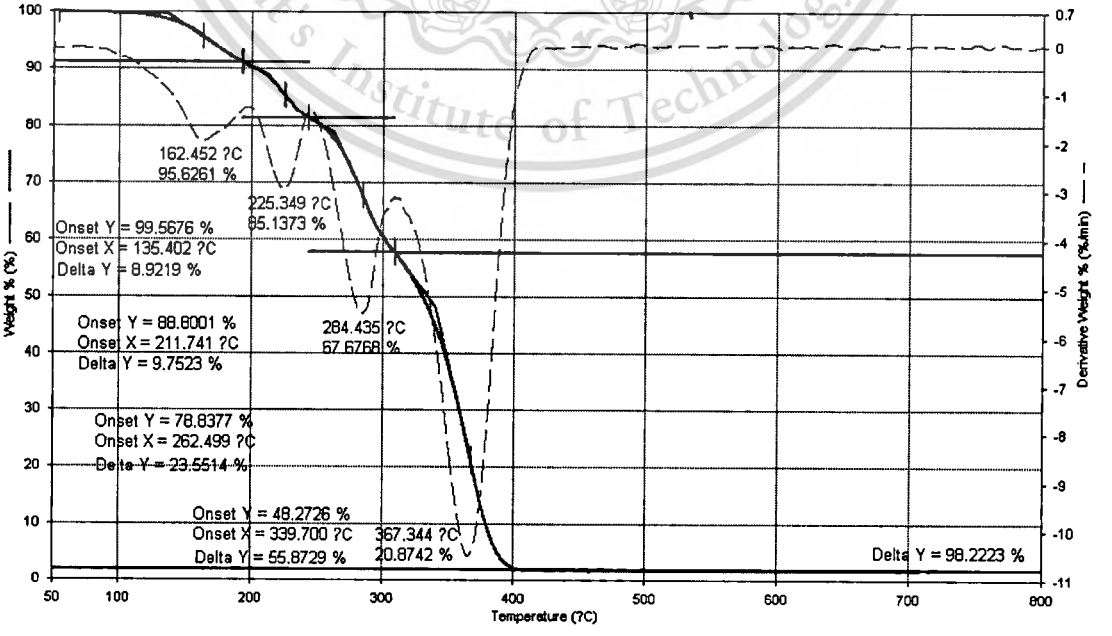

Fig. C-2 Thermogram of PMMA/1% P-MMT film

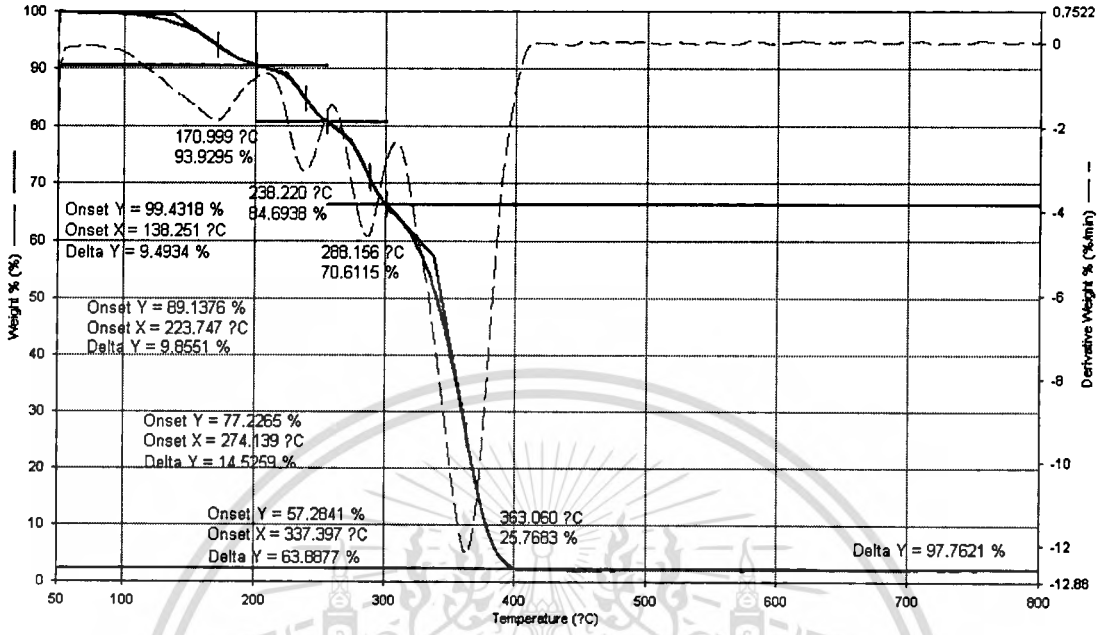

Fig. C-3 Thermogram of PMMA/2% P-MMT film

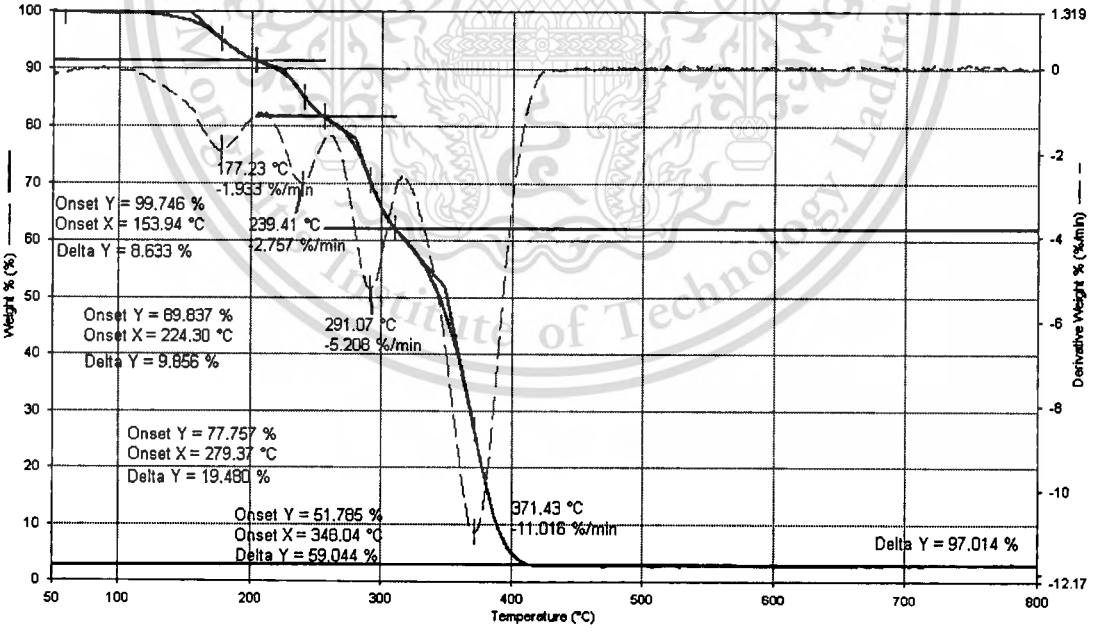

Fig. C-4 Thermogram of PMMA/3% P-MMT film

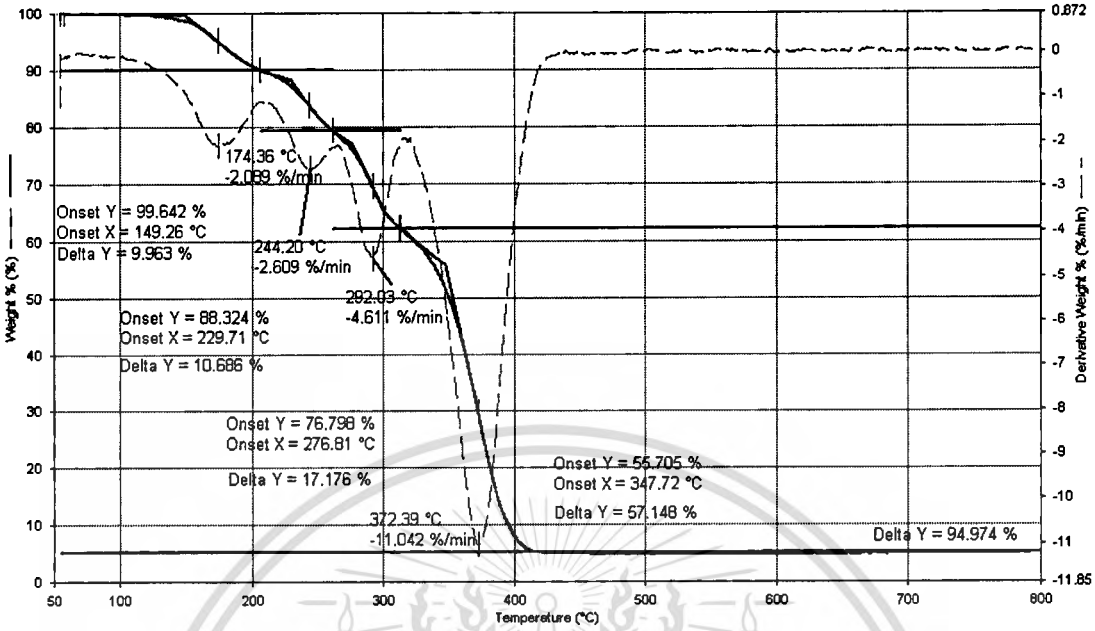

Fig. C-5 Thermogram of PMMA/6% P-MMT film

Appendix-D

The Results of the molecular weight analysis of PMMA by GPC technique

Sample information

Sample Name: PMMA

Vial: 1

Injection: 1

Injection Volume: 100.00 ul

Channel: SATIN

Run Time: 22.00 Minutes

Sample Type: Broad Unknown

Date Acquired: 14/3/08 9:36:53 AM

Acq Method Set:
Y2008_methR_THF_30C_2

Processing Method:
Y2008_ProcR_THF_30C_2

Date Processed: 14/3/08 11:44:19 AM

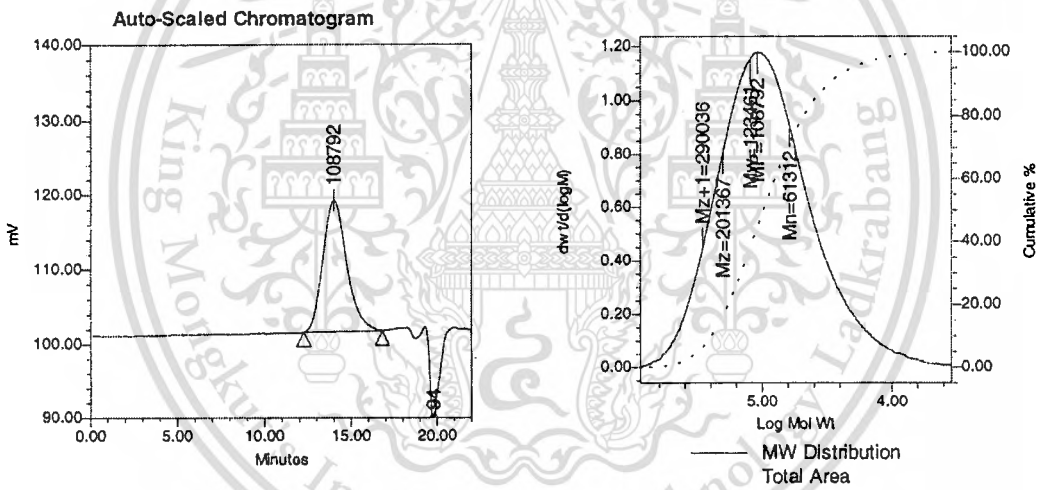

Fig. D-1 Chromatogram of PMMA

Table D-1 Peak Results form chromatogram of PMMA

	Name	MN (g/mole)	Mw (g/mole)	MP	Mz	Mz+1	Polydispersity (MWD)
1	Broad	61312	123461	108792	201367	290036	2.013632
2	Reference			94			

Author Biography

1. **Name** Mr.Sanit sirapanichart

   Date of Birth September, 19th, 1984

   Place of Birth Kalasin

   Education Udonpitthayanukul School, Udontanee

2. **Name** Mr.Suraluck Macksasitorn

   Date of Birth August, 14th, 1986

   Place of Birth Trang

   Education Saravitthaya School, Bangkok

3. **Name** Mr.Suwicha Buakheio

   Date of Birth July, 18th, 1985

   Place of Birth Bangkok

   Education Suksanareewittha School, Bangkok